VOL. LIII, NO. 9, SEPTEMBER, 1958

THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLISHED MONTHLY BY
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1. SCOPE

1.1 This method is intended for use on finished upper leather for shoes or similar end use, or the leather article such as shoe, hand bag, etc.

2. APPARATUS

2.1 Air-tight oven at 120°F.

2.2 Four 2-inch squares of bleached cotton sheeting (ASTM Specification D 503-48T). This material contains less than 0.5% sizing and has a thread count of 186 threads per square inch.

2.3 Two glass plates 6 inches square and 1/8 inch thick.

3. PROCEDURE

3.1 Place the unfinished side of the leather specimen, four inches square, on the center of one of the glass plates. Thoroughly soak the four squares of cotton sheeting in distilled water for five minutes. Stack them on top of each other on the other glass plate. Invert this plate with the cotton cloths, and place on top of the other plate holding the leather specimen. The cloths should line up approximately in the center of the leather specimen. The cloth in immediate contact with the leather is marked #1, the next cloth #2, the next #3, and the top cloth #4. Place this entire sandwich in an oven at 120°F. for twelve hours (overnight). Remove the glass plates and observe the individual cloths for discoloration.

4. RESULTS

4.1 *Migration of bleeding.* Observe each of the four cloths for coloration and report migration as none, 1, 2, 3, or 4, the numbers indicating the cotton cloth that discoloration has reached by migration.

4.2 *Hue.* Note the predominant hue of the colors which bled on each cloth.

4.3 *Intensity.* Observe only cloth #1 for this purpose. The degrees of intensity shall be termed none, slight, moderate, or considerable.

ALCA Provisional Method, 1957.

The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII SEPTEMBER 1958 No. 9

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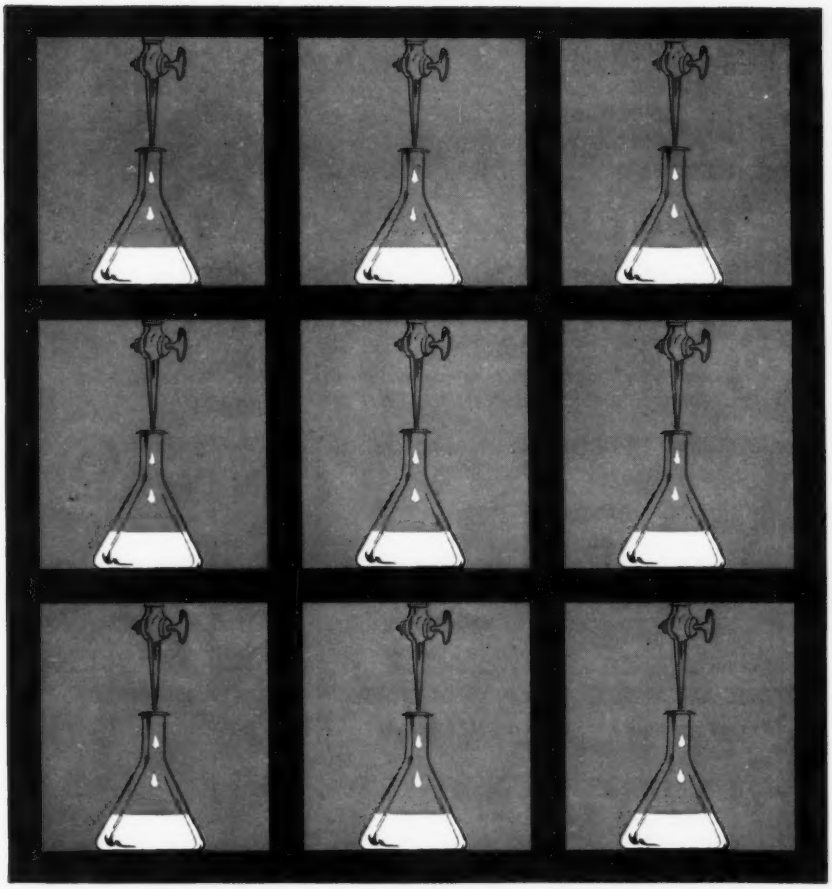

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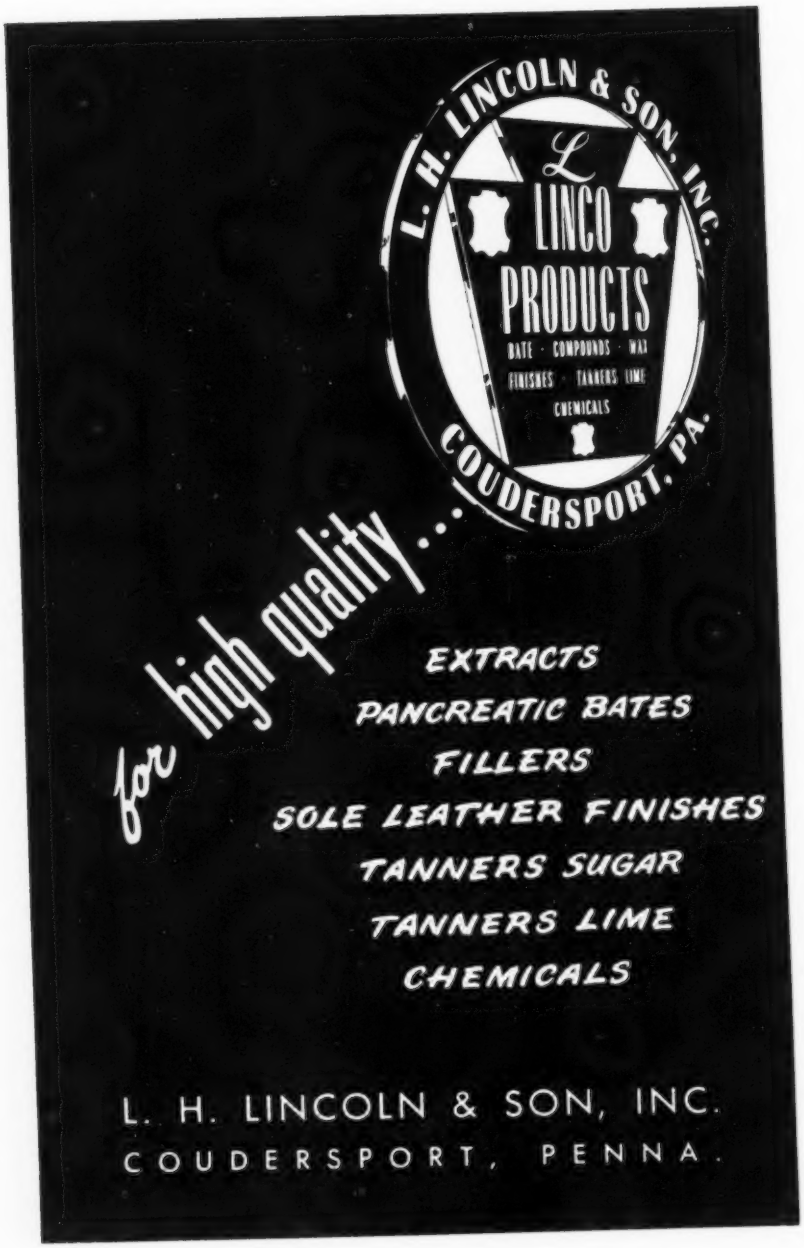
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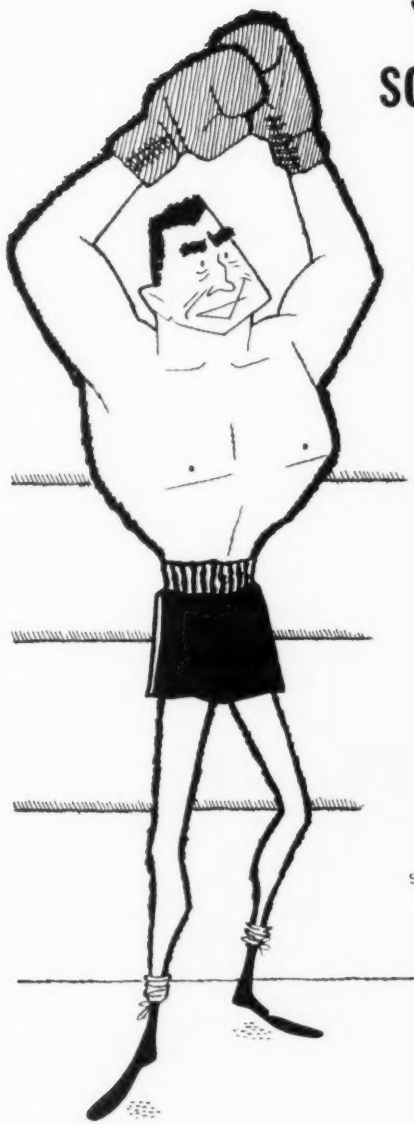

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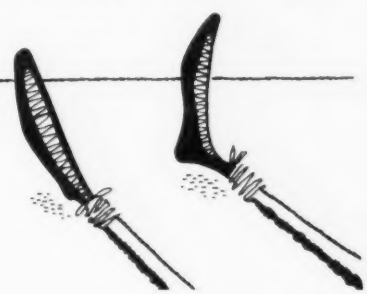

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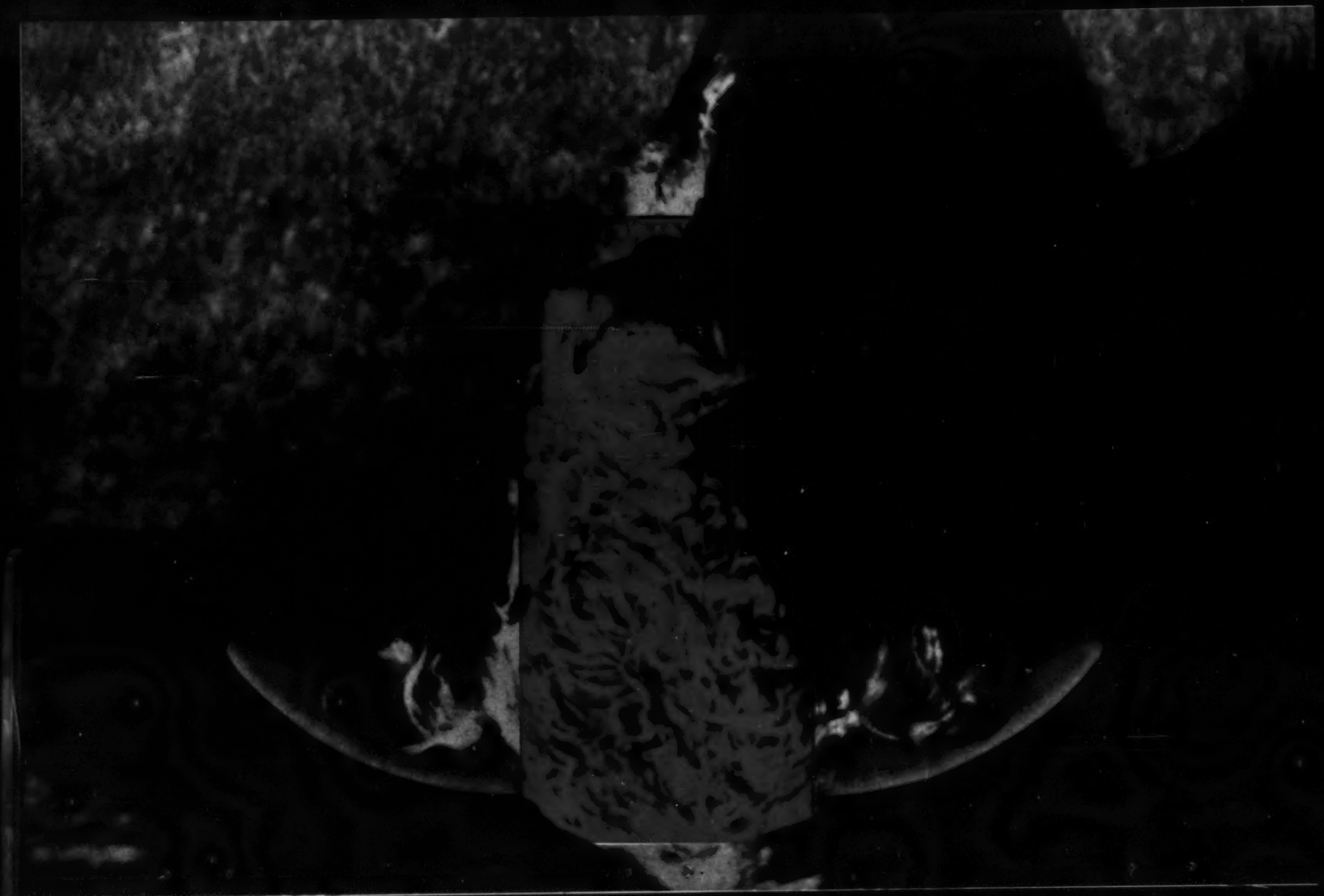

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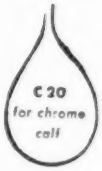

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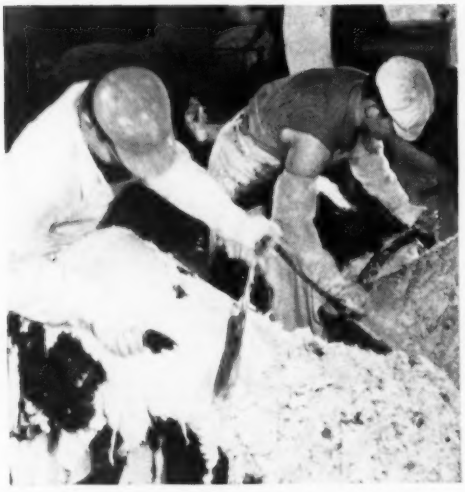

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Bul. 505–Sodium Tetrasulfide for the Leather Industry.
Bul. 508–Action and Use of Sodium Sulfide and Sodium Sulfhydrate in Unhairing Hides and Skins.

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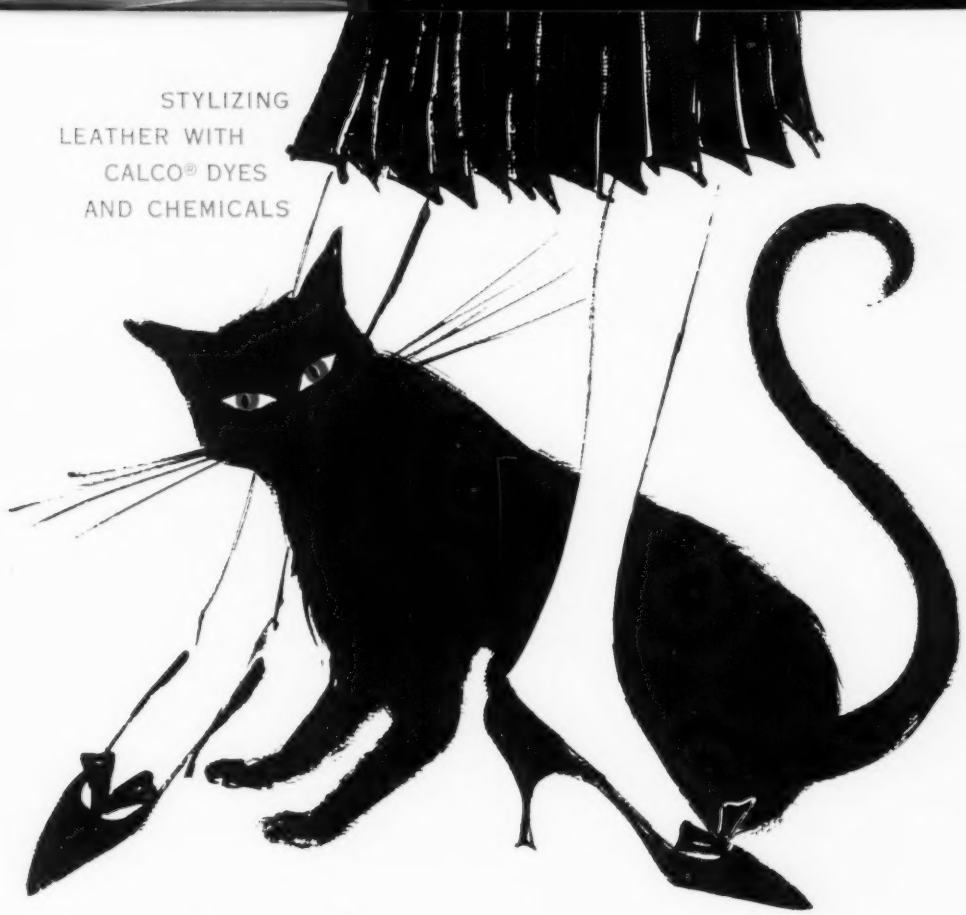

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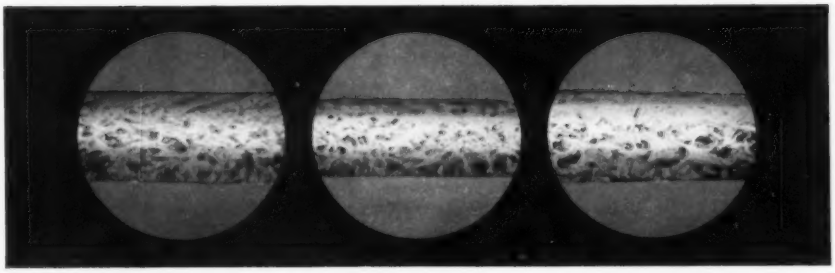

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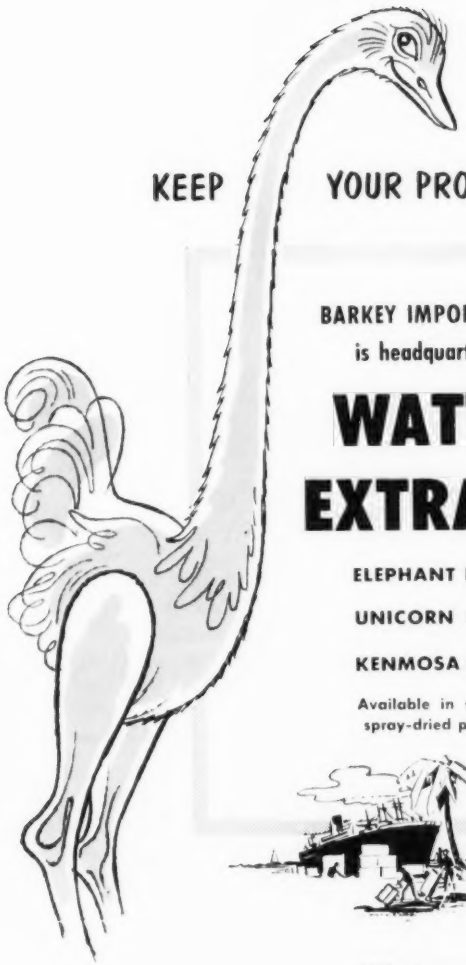

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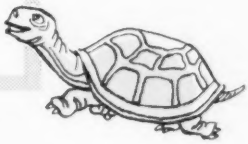

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THE REACTIVITY OF KERATIN*

J. B. Speakman

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Leeds, England

INTRODUCTION

There are many interesting analogies between keratin and collagen, but the chief reason for discussing the reactivity of keratin before an audience of leather chemists is that wool, like leather, is encountering increasingly severe competition from an expanding range of synthetic products. The extent of the competition will be evident from the fact that in 1954 the world production of rayon in both continuous filament and staple fiber form was roughly double the world production of wool, while the production of synthetic fibers, such as nylon, "Terylene", and Orlon, which was negligible before the second world war, was already one-sixth of the world production of wool.

Such a rapid expansion in the production of man-made fibers is, of course, due to many causes. In the case of rayon, the main factor is cheapness, but many of the synthetic fibers, which do not possess a price advantage, owe their success to outstanding properties. Because of its unusually high resistance to abrasion, nylon, for example, was soon used as continuous filament yarn to reinforce the toes and heels of men's socks. Alternatively, nylon staple fiber is blended with wool in the manufacture of knitting yarn, and the displacement of wool is then far more serious. But the greatest challenge to the use of wool in men's socks comes from the development of several methods of bulking continuous filament nylon yarn. Such yarn confers extensibility and softness on the socks, which still show the high wear-resistance of nylon. Further, since nylon has a low affinity for water, the socks have the advantage of drying quickly after being washed. Through the use of nylon, therefore, men's socks may now be classified among the expanding group of "easy-care" garments.

"Terylene" provides a second example of the same kind; worsted-type fabrics, made from yarns containing roughly equal proportions of Terylene staple fiber and wool, are remarkable for the ease with which they can be given creases that are resistant to both dry-cleaning and washing. In the

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manufacture of pleated skirts, for example, permanent pleats are obtained by forming the fabric into pleats and then steaming for 10 minutes in superheated steam. Whereas the pleats normally imparted to all-wool fabrics disappear in dry-cleaning, those of the wool-Terylene fabric resist washing as well as dry-cleaning, and the housewife is thus able to escape the charges for both dry-cleaning and repleating by choosing a wool-Terylene pleated skirt, which she can wash herself, instead of the all-wool skirt. Similarly, in the manufacture of men's trousers, creases which resist dry-cleaning and washing are obtained merely by steaming the wool-Terylene fabric for a few seconds in the Hoffman press.

For a third example we may turn to Orlon, which, like Terylene, has little affinity for water. Knitted garments made of Orlon can, therefore, be dried quickly after being washed, and because the component fibers absorb little water during laundering, the garments preserve their shape during the process. They, also, may be classified as "easy-care" fabrics, and their challenge to wool is enhanced by the fact that the handle of the fabrics resembles that of corresponding all-wool products.

From these three examples it will be evident that the newer man-made fibers have transformed the consumer's conception of what is to be expected of textile materials as regards serviceability. The challenge to wool is severe. It cannot be met by reiterating the advantages of wool as a textile fiber, great though they are. It must be met by focussing attention on the weaknesses of wool and devising methods of correcting them. The purpose of this paper is to outline the recent progress in this field, in the hope that it may encourage the leather chemist in his own closely related battle with substitutes.

The methods which have been evolved for modifying the properties of wool to practical advantage are of four main kinds. In order of decreasing commercial development these are: (*a*) breakdown of cross linkages (disulfide bonds) between the polypeptide chains; (*b*) formation of new cross linkages between the polypeptide chains; (*c*) synthesis of polymers on or within the fibers; and (*d*) formation of cross linkages between the reactive side chains of keratin and those of the polymer synthesized within the fibers. Progress in all these fields of research, especially in the last three, has been handicapped by the almost complete absence of information about the order in which the amino acids are embodied in the polypeptide chains, about differences in composition between the crystalline and amorphous regions of keratin, and about the relative proportions of crystalline and amorphous material. It has, however, been shown recently that there is an overwhelming preponderance of amorphous material in keratin (1), and the various lines of evidence which converge to provide a convincing proof of striking differences in composition between the crystalline and amorphous phases will now be summarized.

DIFFERENCES IN COMPOSITION BETWEEN THE CRYSTALLINE AND AMORPHOUS PHASES OF WOOL KERATIN

Progress in this enquiry has been greatly facilitated by the work of Smith and his collaborators (2) on the compositions of the crystalline and amorphous phases of natural silk. When a solution of silk prepared by the technique of Coleman and Howitt was subjected to the action of pancreatic enzymes at pH 7.8 and 40°C., a precipitate began to form after about 20 minutes, 55% of the original fibroin nitrogen being precipitated after about 24 hours. Amino acid analysis of the soluble and insoluble fractions as well as of the unfractionated fibroin gave the results shown in Table I.

TABLE I

MIXED ENZYME HYDROLYSIS

Amino Acid Residue	Amount (g/100 g) Present in		
	Fibroin	Soluble Fraction	Insoluble Fraction
Glycine	31.4	24.6	38.8
Alanine	26.3	21.6	31.2
Serine + Threonine	16.3	11.8	20.8
Total	74.0	58.0	90.8
Tyrosine	10.3	19.1	2.3

The insoluble fraction, which contains the highest proportion of the amino acids with short side chains and the smallest proportion of bulky tyrosine side chains, was shown by X-ray examination to be highly crystalline and identical in structure with the crystalline regions of silk. Separation of the insoluble fraction is due mainly to the action of chymotrypsin in breaking the polypeptide chains at each tyrosine unit, thus giving fragments which, since they consist mainly of amino acids with short side chains, can associate readily with one another. In the case of silk, therefore, the amorphous regions contain and are created by amino acid residues with bulky side chains, while the crystalline regions consist of amino acid residues with small side chains. In connection with later argument about the crystalline and amorphous phases of keratin, it is interesting to note that Smith and his collaborators (4) have been able to correlate the shapes of the load-extension diagrams of different varieties of silk with the proportions of amino acids with long side chains that they contain; the silks are placed in the same order—Tussah, Bombyx, Anaphe—as regards both ease of extension and content of amino acids with long side chains.

In the light of these results, the crystalline and amorphous phases of keratin may be expected to consist preferentially of amino acids with short and long side chains, respectively, and there is much evidence to support this view. Taking the amorphous phase first, it has been shown that the load-extension diagrams of human hair are coincident at extensions above 35% in water and 0.1*N* hydrochloric acid (5). According to Astbury and Woods (6) the onset of the α—β transformation, i.e., the extension of the crystalline phase of wool, is first perceptible at 20% extension, the transformation proceeding with increasing extension up to the breaking point, when little of the α-form is present. The salt linkage breakdown which is responsible for the weakening of animal fibers in acid at extensions below 35% must, therefore, take place in the amorphous phase. In other words, the amino acid residues of lysine, arginine, aspartic acid, and glutamic acid are present in the amorphous phase but not in the crystalline phase. A further indication that the whole of the lysine in wool is present in the amorphous phase is to be found in the fact that complete reaction with 1-fluoro-2:4-dinitrobenzene is obtained in 48 hours at 40°C. and pH 7.0 (7). Similarly, since 96% of the tyrosine of wool can be converted into 3:5-di-iodotyrosine by treatment with a solution of iodine in ethanol for 72 hours at 22.2°C. (8), the bulky tyrosine side chains must be found mainly in the more readily accessible and, presumably, amorphous regions of the fiber, just as in the case of silk.

There is thus much evidence to indicate that the amorphous regions of wool contain and are created by the amino acids with bulky side chains, and the crystalline regions must, therefore, be rich in amino acids with short side chains. As yet, however, little precise information is available about the composition of the crystalline phase, though there appears to be some significance in the results obtained by Consden and Gordon (9) in their study of partial hydrolyzates of wool. When wool is hydrolyzed with acids under mild conditions, it is to be expected that the more accessible amorphous regions of the fiber will be more vulnerable and that the peptides present in the partial hydrolyzates will be derived preferentially from the crystalline phase, though the effect of the amino acid environment on the reactivity of the peptide bonds cannot be ignored. Consden and Gordon hydrolyzed wool with 10*N* hydrochloric acid for 10 days at 37°C., and after separating the acidic peptides, treated the remainder with bromine and separated the fraction containing peptides of cysteic acid. In relation to the preceding argument it is interesting that the amino acids with short side chains, which constitute the crystalline phase of silk, should preponderate so heavily in the partial hydrolyzate, as shown in Table II, especially as peptide bonds involving the amino group of serine are particularly labile.

The general weight of evidence seems, therefore, to support the theory that the crystalline and amorphous regions of keratin are rich in amino acids with short and long side chains, respectively. But perhaps the main

support for the theory comes from the fact that it serves to explain many puzzling features of the reactivity of keratin.

TABLE II

Amino-acid combined with cysteic acid		Amount combined with cysteic acid (arbitrary units)
Glycine		34
Alanine		44
Serine		60
Threonine		40
	Total	178
Valine		20
Leucine		18
Phenylalanine		4
Proline		none
	Total	42

BREAKDOWN OF DISULFIDE BONDS BETWEEN THE PEPTIDE CHAINS

During the past 25 years all constructive attempts to modify the properties of wool to commercial advantage have been based on the simple conception that the fiber consists of polypeptide chains bridged by cystine and salt linkages. In the case of processes which depend for their success on disulfide bond breakdown, differences in composition of the crystalline and amorphous phases are of little consequence, and it is in this field that most of the advances have been made. The discovery (10) that any reagent which is capable of causing disulfide bond breakdown without at the same time forming new cross linkages between the peptide chains can, if it is applied under conditions which restrict its action to the surface of the fibers, render the surface scale structure inoperative, has led to the development of a series of new processes for making wool fabrics unshrinkable. Such processes, many of which leave the handle of the wool unimpaired, have ensured the continued use of wool in hosiery fabrics by correcting one of its main defects. More recently (11) it has been shown that the reaction between disulfide bonds and sodium bisulfite may be used to impart pleats to all-wool fabrics which are just as resistant to dry-cleaning and washing as the pleats of wool-Terylene mixture fabrics, to which reference has already been made. During the last wet process in finishing, the wool fabric is treated with a 1% solution of sodium bisulfite at room temperature, when some of the disulfide bonds are broken:

$$\text{R-S-S-R} + \text{NaHSO}_3 \longrightarrow \text{R SH} + \text{R-S-SO}_3\text{Na}$$

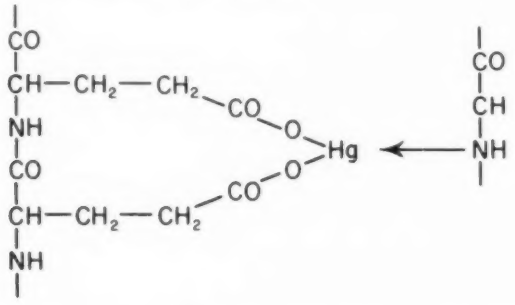
The fabric is then rinsed to remove the excess bisulfite and dried at a low temperature. As supplied to the pleater, the fabric is indistinguishable from the untreated fabric, and pleating is carried out in the usual way, i.e., by forming the fabric into pleats between pleating papers and then steaming for 20 minutes. During the steaming process, disulfide bonds are re-formed by reversal of the above reaction, and since bond re-formation takes place with the fibers held in a state of deformation, the deformed state is the permanent one. The pleats obtained in this way are totally resistant to dry-cleaning, and it has been found that a pleated skirt can be immersed in water for a period of up to at least 10 days without loss of pleats. It is thus unnecessary to blend Terylene with wool in order to obtain fabrics which are capable of being pleated permanently, and the new process, besides improving the competitive power of wool in relation to man-made fibers, takes the all-wool fabric a stage further towards the "easy-care" type of fabric which is now desired by the consumer.

From these examples alone it will be evident that wool has little to fear from man-made fibers if full advantage is taken of its reactivity. But it is when attention is transferred from disulfide bond breakdown reactions to cross-linking reactions that progress is found to be handicapped by lack of knowledge of the nature and arrangement of the amino acids in the crystalline and amorphous phases of keratin.

CROSS-LINKING REACTIONS

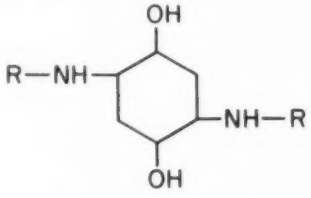
Since the basic and acidic side chains of keratin are present in the amorphous phase, they must be readily accessible to cross-linking agents. Formaldehyde, which reacts with basic and amide side chains was, therefore, expected to be capable of strengthening animal fibers, but treatment for 48 hours with a 0.732% solution at the optimum pH of 6–7 gave only a 4.5% increase in the resistance of the human hair fibers to 30% extension in water (12). Similarly, when the acidic side chains are cross-linked with di-epoxides, the strengthening effect is small; human hair fibers treated with a 4% (v/v) solution of 3:3-isopropylidene 1:2-5:6-dianhydromannitol for 24 hours at pH 4.4 and 50°C. showed an increase in resistance to 30% extension in water of only 7.8% (13). It has been customary to assume that the poor strengthening effect of formaldehyde is due to the inability of a small molecule to bridge the distance between the reactive side chains, but no such explanation can be offered in the case of di-epoxides, for the molecules are larger. A much more reasonable explanation, now that the basic and acidic side chains are known to be present in the amorphous phase, is that cross linking is unlikely to have a profound effect on the elastic properties of a disorganized structure unless it occurs with very great frequency. How frequent the cross linking must be is well indicated by the remarkable extent to which animal fibers may be strengthened by reaction with mercuric acetate; after

being treated with a solution of mercuric acetate (0.1*M*) in acetic acid (0.1*N*) for 16 hours at 22.2°C., the resistance of Lincoln wool fibers to 30% extension in water was increased by 36% (14). The amount of mercury which combines with the keratin to produce this effect is at least 220 milliequivalents per 100 g. dry wool (15). Since glutamylglutamic acid is the most abundant acidic dipeptide in partial hydrolyzates of wool (16), and since mercury coordinates readily with nitrogen compounds, it seems probable that cross linkages of the following type:



play an important part in reinforcing wool fibers to the extent which is necessary if valuable technical effects, such as the unshrinkability which is based on modified elastic properties of the fibers, are to be obtained. Wherever and however the mercury combines with reactive side chains, nitrogen atoms are always likely to be within easy reach, and it is on the ability to coordinate with nitrogen compounds that the effectiveness of mercuric acetate as a cross-linking agent really rests.

All the preceding observations, and especially the striking difference in effectiveness of formaldehyde and mercuric acetate as cross-linking agents, combine to show that very frequent cross linking is essential for the reinforcement of the disorganized amorphous regions of keratin. At first sight, therefore, it is surprising that benzoquinone, which is believed to cross-link basic side chains as follows:



should be so much more effective than formaldehyde in reinforcing animal fibers; when human hair fibers were treated with a 1% solution in a 5%

(v/v) alcohol for 48 hours at 50°C. and pH 4.7, the increase in resistance to 30% extension in water was 20% (12). In order to explain this result it has been assumed that benzoquinone is able to cross-link more of the basic side chains than formaldehyde because of the greater size of the molecule. This explanation has now been found to be untenable (17).

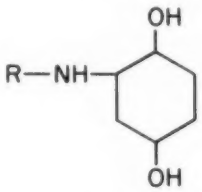
Doubt about the formation of covalent cross linkages when wool is treated with benzoquinone was first aroused by the discovery that fibers which had been treated with a 1% solution of benzoquinone in 12.5% (v/v) alcohol for 48 hours at 50°C. and pH 4.96 contracted to a length 30% less than the original length as a result of extraction with the constant-boiling mixture of pyridine and water for 4 hours in a Soxhlet apparatus. Untreated wool fibers did not supercontract under similar conditions, and the treated fibers should have been even more resistant if they are as heavily cross-linked as the increase in resistance to deformation suggests. If, however, benzoquinone reacts with basic side chains without forming covalent cross linkages, supercontraction is likely to be promoted because deaminated fibers, for example, supercontract in boiling solutions of borax and sodium sulfite, whereas untreated fibers do not. Further studies of the supercontraction of benzoquinone-treated fibers were therefore undertaken.

After being treated with benzoquinone under the above conditions, approximately 5-cm. lengths of Lincoln wool fibers were mounted in stainless steel setting frames. By screwing the top clamp of each frame upwards, the fiber was drawn exactly taut, and its precise length was measured by means of a travelling microscope. After the fiber had been slackened by screwing the top clamp downwards, the instrument was immersed for 1 hour in a boiling solution of the appropriate reagent. At the end of this time the fiber was washed in three changes of distilled water, dried in complete absence of tension, and again drawn taut so that its length could be remeasured. Corresponding experiments were carried out with untreated fibers, and values for the supercontraction given by (*a*) 2% borax, (*b*) 5% hydrated sodium sulfite and (*c*) 5% sodium metabisulfite solutions are given in Table III, each value being the mean of 4–6 results.

TABLE III

Reagent	Percentage Supercontraction	
	Untreated Fibers	Benzoquinone-treated Fibers
Borax	− 0.2	18.1
Sodium sulfite	0.7	31.1
Sodium metabisulfite	32.1	26.2

When a reagent forms stable covalent cross linkages between the polypeptide chains of wool, supercontraction in a boiling solution of sodium bisulfite is prevented, and the fact that benzoquinone-treated fibers do supercontract to a marked extent suggests that they contain few, if any, new cross linkages. Benzoquinone must, however, react with the basic side chains, because the treated fibers, like deaminated fibers, supercontract in boiling solutions of borax and sodium sulfite. But reaction with basic side chains to give side chains of the following type:



can hardly account for the marked increase in resistance to extension of benzoquinone-treated fibers. Part of the increase was found to be due to the formation and deposition of a loose polymer of benzoquinone in the fibers during the 48 hours of treatment at 50°C.

A 2.5-g. pattern of all-wool flannel, which had been purified by extraction with alcohol and ether, followed by washing in distilled water, was treated with the solution of benzoquinone under the usual conditions, the liquor:wool ratio being 50:1. The pattern was then washed and dried, the gain in dry weight being 16.46%. It was found that the most suitable solvent for extracting polymer from the fibers is the constant-boiling mixture of pyridine and water. The pattern was extracted with the mixture under three successive conditions of increasing severity, and the amounts of extract, dried over concentrated sulfuric acid and then over phosphorus pentoxide *in vacuo*, are given in Table IV, which includes corresponding values for untreated flannel.

TABLE IV

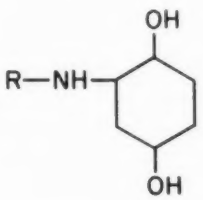
Extraction Conditions	Amount of Extract (% *on dry weight of untreated flannel*)	
	Untreated Flannel	Treated Flannel
100 ml., 4 hr. at 25°C.	0.18	5.65
100 ml., 2 hr. at 50°C.	0.09	1.75
Soxhlet, 4 hr.	5.08	2.50
Total	5.35	9.90

Extraction with the hot mixture causes severe degradation of the wool, as is indicated by the high value of the extract from the untreated flannel, but the bulk of the loose polymer can be removed from the treated flannel at 25°C. The effect of extraction for 4 hours at 25°C. on the resistance of the treated and untreated fibers at 30% extension in water at 22.2°C. is shown in Table V.

TABLE V

Fibers	Change in Resistance to Extension %	
	Before Extraction	After Extraction
Benzoquinone-treated	24.4	11.6
Untreated	——	− 1.8

It is clear, therefore, that about half [24.4 − (11.6 + 1.8) = 11.0] of the increased resistance to deformation of the benzoquinone-treated fibers is due to a loose deposit of polymer. Extraction of polymer from the few fibers used in this experiment was undoubtedly more complete than with the flannel (Table IV), because the same volume of solvent was used in both cases, but it is in any case obvious that the whole of the increased resistance to deformation of the benzoquinone-treated fibers cannot be referred to the combination of each basic side chain with one molecule of benzoquinone. The maximum increase in weight to be expected on this basis is 8.64%, and in agreement with earlier observations (18) it has been found that reaction with the basic side chains is incomplete. Since the observed gain in weight of the wool, after deducting the amounts of polymer extracted at 25° and 50°C., is 9.06%, it seems reasonable to conclude that more than one molecule of benzoquinone combines with each of the basic side chains involved in the reaction. This conclusion is all the more reasonable because the weights of the extracts from the treated flannel (Table IV) are all too high, owing to the presence of combined pyridine as well as protein, as is shown by the fact that the fall in dry weight of the flannel was only 8.53% compared with 9.90% for the combined weights of the extracts. It seems probable, therefore, that after



side chains have been formed by reaction with one molecule of benzoquinone, the new side chains take part in polymerization with more quinone, thus forming a graft copolymer of protein and quinone. The graft copolymer, through hydrogen bonding as well as steric hindrance, will cause a profound alteration in the elastic properties of the fibers and is regarded as being the second factor responsible for the increased resistance to deformation of benzoquinone-treated fibers in water.

POLYMERIZATION REACTIONS

Three methods of synthesizing polymers inside wool fibers have so far been developed in these laboratories. They involve (*a*) treatment with the vapors of water and monomer (19); (*b*) applying a solution containing hydrogen peroxide and monomer to wool containing ferrous ions (20); and (*c*) treatment with a solution containing potassium persulfate and monomer (21). In the case of polymethacrylamide subsequent treatment with formaldehyde leads to the formation of a graft copolymer (20), but in the absence of some such reaction the bulk of the polymer seems to be a loose deposit. Because it is loose, the increased resistance to deformation of the treated fibers does not survive repeated extension, as in the case of polyethylene sulfide (19). In the light of the preceding work on the action of benzoquinone on wool it seemed probable that more effective alteration of the elastic properties of the fibers could be obtained with smaller amounts of polymer, if the latter were anchored to the fiber as a graft copolymer. Three lines of attack on this problem are being pursued.

Oxidation polymerization.—In this case it was hoped that anchoring of the polymer would be realized through the free radicals formed in the course of polymerization. The reaction chosen for examination was the formation of pigments by oxidizing *p*-phenylene diamine with hydrogen peroxide.

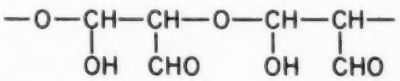
Six Lincoln wool fibers which had been calibrated by determining their load-extension curves up to 30% extensions in distilled water at 22.2°C. were attached to a 2.5-g. pattern of purified flannel, and then steeped for 24 hours at 25°C. in 125 ml. of a solution containing hydrated copper sulfate (0.4%) and acetic acid (0.2%). After the pattern had been rinsed in three changes of distilled water, it was immersed in 125 ml. of a pH 8 buffer solution containing *p*-phenylene diamine (1.25 g.) for 10 minutes before adding 17 ml. of 3.4% (v/v) hydrogen peroxide. The reaction was allowed to proceed for 24 hours at 25°C., and the pattern was then removed and washed in running water overnight before the fibers were separated for restretching. The average increase in resistance to extension of the fibers was 18.1%, and the gain in dry weight of the pattern was 12.30%. When the pattern was extracted with the constant-boiling mixture of pyridine and water, much of the pigment was easily removed, as is shown by the data of Table VI.

TABLE VI

Extraction Conditions	Amount of Extract (% on dry weight of untreated wool)	
	Untreated Flannel	Treated Flannel
100 ml., 4 hr. at 25°C.	0.18	6.79
100 ml., 2 hr. at 50°C.	0.09	1.51
Soxhlet, 4 hr.	5.08	5.02
Total	5.35	13.32

After the series of extractions the treated pattern was still highly colored, and the fact that the total amount extracted (13.32%) exceeds the original gain in weight (12.30%) is, of course, due to the loss of protein. Since, however, so much of the pigment is easily extracted, and since the remainder seems to be incapable of giving any notable protection of the protein against dissolution by the hot constant-boiling mixture (compare Table IV and Table VI), it seems clear that the action of the pigment in increasing the resistance of the fibers to extension is due mainly to the steric effects of a loose deposit of polymer. Part of the pigment may be present as a graft copolymer, but the amount cannot exceed 4% (12.30 − 8.30) and is likely to be much smaller. Attention was, therefore, turned to other possible means of forming graft copolymers.

The action of reductone (22) on keratin (23).—The principle underlying these experiments is that of using a polymerizable compound which is capable also of forming covalent bonds with keratin. Reductone was chosen because it should be capable of combining with basic side chains, and it polymerizes with great ease to give a polymer which is believed, on the basis of evidence that will be reported elsewhere, to have the following constitution:



When human hair fibers were treated with a mixture of reductone (0.5 g.) and water (5 ml.) for 48 hours at 25°C., the increase in the resistance of the fibers to 25% extension in water was 54%. A 0.1 g. sample of Lincoln wool treated with the same amount of the aqueous solution of reductone under the same conditions showed an increase in dry weight of 60.3%. It seems probable that the polymer formed at 25°C. is loosely deposited within the fibers, because the marked strengthening does not survive the first extension of the treated fiber. When, however, the reaction is carried out at 50°C.,

the strengthening survives repeated extension, and the polymer, unlike that formed at 25°C., is almost completely resistant to extraction by 0.1*N* hydrochloric acid. Since von Euler *et al.* (24) have shown that reductone reacts with *p*-nitroaniline to give the following compound:

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CH = C(OH) \cdot CHO,$$

and since treatment with reductone causes no change in weight or resistance to extension with deaminated wool and hair, it seems safe to conclude that a graft copolymer is formed when wool reacts with reductone at 50°C., the structure being reinforced by combination of the aldehyde groups of the polymer with reactive side chains of the polypeptide chains as well as by hydrogen bonding and steric hindrance.

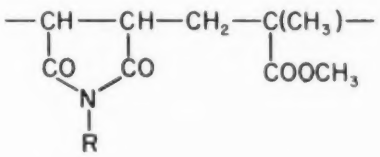
Copolymers with combined maleic anhydride (25).—The third attempt to form graft copolymers arose out of the discovery that wool can be protected against heat treatment by introducing unsaturated compounds into the fibers (26). When, for example, an all-wool flannel was treated with maleic anhydride, which combines with the basic side chains of keratin, subsequent heating in an atmosphere of dry nitrogen for 24 hours at 150°C. gave a fabric which was much more resistant to dissolution in sodium hydroxide and urea-bisulfite solutions than the heated untreated flannel. Data for samples of flannel containing different amounts of maleic anhydride are given in Table VII, which includes corresponding data for one sample containing succinic anhydride.

TABLE VII

Combined Maleic Anhydride (*millimols per g. dry wool*)	Alkali Solubility (%)	Urea-Bisulfite Solubility (%)
—	13.5	13.9
0.08	8.1	6.9
0.17	6.8	1.3
0.45	4.6	− 2.5
0.65	2.6	− 4.9
0.86	0.7	− 7.9
1.12	− 1.1	−11.2
1.10 (succinic anhydride)	81.5	32.2

Comparison of the results for maleic and succinic anhydride suggests that the protective effect of the former is due to the formation of addition compounds, and, therefore, new cross linkages, with thiols derived from the breakdown of disulfide bonds under the influence of heat.

In the light of these results it seemed probable that graft copolymers might be formed easily by applying vinyl compounds to wool previously treated with maleic anhydride. Preferential internal polymerization of the monomer may be brought about in several ways (19–21), and a graft copolymer of the following type is obtained:



By varying the nature of the monomer a wide variety of properties can, of course, be conferred on the reinforced fibers.

The importance of graft copolymerization is not, however, confined to reactions which take place preferentially in the amorphous phase. It has already been shown (27) that one of the most promising methods of modifying the properties of wool is by forming an anchored film of polymer on the surface of the fibers; with anhydrocarboxyglycine dimensional stability, unshrinkability, and greatly increased resistance to wear were obtained with no more than 3% by weight of polymer. Despite its advantages little use has been made of the method because anhydrocarboxyglycine is not available in commercial quantities. Fortunately, other methods of achieving the same end are now available. If, for example, flannel is impregnated with a solution of maleic anhydride in an inert organic solvent and then heated for 30 minutes or longer at 85°C., subsequent impregnation with a solution of methyl methacrylate and benzoyl peroxide (0.5% on the weight of monomer) in an inert organic solvent, followed by heating at the same temperature, leads to the formation of an anchored film of copolymer on the surface of the fibers.

CONCLUSION

In conclusion, therefore, the general argument of this paper may be summarized as follows: The wool fiber contained such a high proportion of disorganized, amorphous material that simple cross-linking reactions are unable to modify the properties of wool to an extent which is commercially useful unless the reagent is polyfunctional and capable of reaction with groups which occur with great frequency in the fiber. One such reagent is mercuric acetate, which owes its success to the ease with which mercury salts coordinate with nitrogen-containing compounds. A much more promising method of producing chemically modified wools is by processes which lead to the formation of graft copolymers inside or outside the fibers, and a general method of achieving this end has been outlined. Through its use should

come new methods of increasing the resistance of wool to shrinkage, wear, chemical attack, and microbiological attack, and the ability to confront an expanding range of man-made fibers with equanimity.

ACKNOWLEDGMENT

The author and his colleagues are indebted to the International Wool Secretariat for grants in aid of these investigations.

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The salient fact regarding leather manufactures was their quantitative importance. In value of output boot and shoe making ranked fifth among our manufacturing industries; and if we disregard duplications common to all such statistics, caused by the appearance of the products of one branch of industry as the raw materials of another, leather and leather articles were exceeded in value only by flour and by unmanufactured and manufactured iron.

— *History of Manufactures in the United States*, Vol. I, 1607–1860. Victor S. Clark. New York: McGraw-Hill Book Company, Inc., 1929.

DEGRADATION OF COLLAGEN BY HEAT*

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ABSTRACT

Purified steerhide collagen heated at temperatures ranging from 125° to 170°C. in vacuum, air, and oxygen for periods of 3 days shows reduced capacity to adsorb water vapor and increased solubility in water. Small changes are apparent in the infrared spectra of the most severely degraded materials. Losses in the amounts of a number of amino acids as the temperature of heating is increased are shown by quantitative paper-chromatographic analysis. In particular, methionine, serine, threonine, and tyrosine are affected. Collagen heated in air at 100° C. for 3 days at relative humidities ranging from 20% to 90% shows increased solubility in water but relatively little change in amino acid composition. The water-soluble fractions obtained by heating at high relative humidities are of somewhat higher molecular weight than those obtained by heating in the absence of moisture.

INTRODUCTION

Controlled degradation reactions provide one approach to elucidation of the chemical structure of polymers. In the field of synthetic polymers it has become increasingly evident that certain well defined structural features present in small concentration, such as chain ends, points of branching, and oxygenated groups, are often sites at which degradation reactions are most readily initiated or propagated.

By means of recently developed chromatographic procedures the degradation of a natural polymer such as collagen may be studied with the aim of detecting the parts of the fundamental protein structure most susceptible to attack.

The degradation of leather which occurs during aging has been the subject of numerous reports. Leather consists of two main constituents—a tanning material and hide substance (collagen). Kanagy (1) has postulated that the deterioration of vegetable leather in the presence of oxygen proceeds by two mechanisms, an oxidizing action on the tannins and a hydrolytic attack on the hide substance.

*Presented at the Fifty-third Annual ALCA Meeting, Lake Placid, N. Y., June 4, 1957.

This paper is concerned only with a study of degradation of hide substance or untanned collagen. The effects of thermal degradation in vacuum, air, and oxygen, and in the presence of moisture are discussed.

MATERIALS AND METHODS

The collagen from which the various degradation products were derived was a highly purified material prepared from raw steerhide. The grain and flesh layers of the hide were split off and discarded. The corium was ground to a powder and freed of extraneous fats, salts, and proteins by a series of aqueous and organic extractions (2). The final product was ground in a Wiley mill to pass a 4-mm. sieve.

Collagen was degraded by heating in vacuum, air, and oxygen at 125°-170°C. for 3 days. Dry air and dry oxygen were passed through a glass tube containing the collagen. A vacuum pump was attached to the glass tube for the degradation in vacuum, and the pump was run continuously during the degradation period. Volatile fragments condensed as oily substances in the trap protecting the vacuum pump; these substances were not analyzed. As the temperature was raised, the color of the specimens changed from the white of the parent collagen through yellow to light brown, and finally to dark brown. The more severe the heating, the denser and the more nonfibrous the material tended to become.

Collagen was also degraded by exposure in air at 100°C. for 3 days to relative humidities ranging from approximately 20% to 90%. An inverted, sealed-off U-tube was used in this experiment. The collagen was in one arm of the tube, while a saturated salt solution (with enough excess salt added to insure a saturated solution at the higher temperature) was in the other. This assembly was a sealed, all-glass unit. The unit was placed in an oven at 100°C. with the curve of the U upright. The higher the humidity of exposure, the less fibrous and the darker in color the specimens became.

All the degraded collagens were analyzed for total nitrogen and amino acid content. Total nitrogen was determined by the ALCA official method, using mercuric oxide as a catalyst. The amino acid data, with the exception of those for tyrosine and hydroxyproline, were obtained by a two-dimensional, paper-chromatographic procedure applied to hydrolyzates of the sample, as described in a previous paper (3). Hydroxyproline was determined by the method of Neuman and Logan (4), except that the excess hydrogen peroxide was removed by 20 minutes of severe agitation of test tubes at room temperature. The copper sulfate and sodium hydroxide reagents were mixed before addition as were also the *p*-dimethylaminobenzaldehyde and sulfuric acid. Tyrosine was determined by the colorimetric method of Udenfriend and Cooper (5).

Degraded samples were extracted with water at 23°C., and the nitrogen contents of the soluble fractions were determined. Amino nitrogen and viscosity were also determined on some of the extracts. The Van Slyke manometric equipment was used to determine amino nitrogen. A 5-minute reaction period was found to be sufficient for the amino nitrogen estimation. Viscosity measurements were made with an Ostwald viscometer in a bath at 24°C. Each extract or diluted extract was made 0.2 molar with respect to sodium chloride.

The capacity of the degraded materials to adsorb water vapor at different relative humidities was determined by using the procedure and equipment described by Kanagy (6).

Infrared spectra of several of the degraded materials were obtained by the potassium bromide pellet technique (7). Samples were ground in a Wiley mill, mixed with potassium bromide, and evacuated before pressing.

RESULTS AND DISCUSSION

Thermal degradation in vacuum, air, and oxygen.—A change in the color of most samples was observed. Only the sample heated in vacuum at 150°C. for 3 days retained its natural white color. The samples heated at 125° in oxygen, at 140°, 150°, and 170° in air, and at 170° in vacuum, were yellow; those samples heated at 150° and 170° in a stream of oxygen were brown. Even those samples most severely degraded were still fibrous in appearance.

TABLE I

NITROGEN CONTENT OF COLLAGENS DEGRADED BY DRY HEAT

3-Day Treatment	Nitrogen (*dry basis*) %
Control	18.15
150°—Vacuum	18.16
170°—Vacuum	18.18
140°—Air	18.06
150°—Air	18.12
170°—Air	18.10
125°—Oxygen	18.17
150°—Oxygen	18.30
170°—Oxygen	18.62

Table I shows the nitrogen contents of the heated materials. The nitrogen content of the sample heated to 170°C. in oxygen is significantly higher than that of the parent collagen. The high content of residual nitrogen indicates

that substances containing little or no nitrogen were removed by the heat treatment. Even though the sample heated for 3 days at 170°C. in air lost approximately 4% of its original dry weight, the nitrogen content remained unchanged. On the other hand, the sample heated in oxygen at 170° C. lost slightly more than 7% of its dry weight during the heating process, and the nitrogen content was increased considerably.

The infrared spectrum of the sample heated at 170° C. in air showed several small differences from that of the parent collagen in the region of the spectrum from 7 to 9 microns. These differences were also observed in the sample heated in oxygen at 170° C. The spectra for collagen and for the material heated in oxygen are shown in Fig. 1. Some of the material heated in oxygen at 170° C. was thoroughly extracted with water to remove the bulk of its water-soluble fraction, and an infrared spectrum was obtained on the remaining material after redrying it. No change in the spectrum was observed, even though more than 25% of the total nitrogen had been removed by the water.

TABLE II

EFFECT OF HEATING COLLAGEN TO ELEVATED TEMPERATURES FOR 3 DAYS IN VACUUM, OXYGEN, AND AIR

Amino Acid*	Loss in Amino Acids, %**							
	170°			150°			140°	125°
	Vac.	Air	O_2	Vac.	Air	O_2	Air	O_2
Methionine	40	100	100		40	50	30	14
Threonine	48	48	84	20	40	48	12	33
Serine	50	58	66	34	37	40	18	15
Tyrosine	20	40	65		15	34	20	12
Arginine	19	37	51	16	11	16		
Phenylalanine	24	17	39	20	14	30		
Lysine plus hydroxylysine	22	39	35	18	27	33	16	11
Valine	23	23	27	23	20	21		11
Leucine plus isoleucine			29			26		
Hydroxyproline			32					
Glutamic Acid								
Aspartic Acid								
Glycine								
Proline								
Alanine								

*Arranged downward in approximately increasing order of stability.
**Blanks in the table indicate losses of less than 10%.

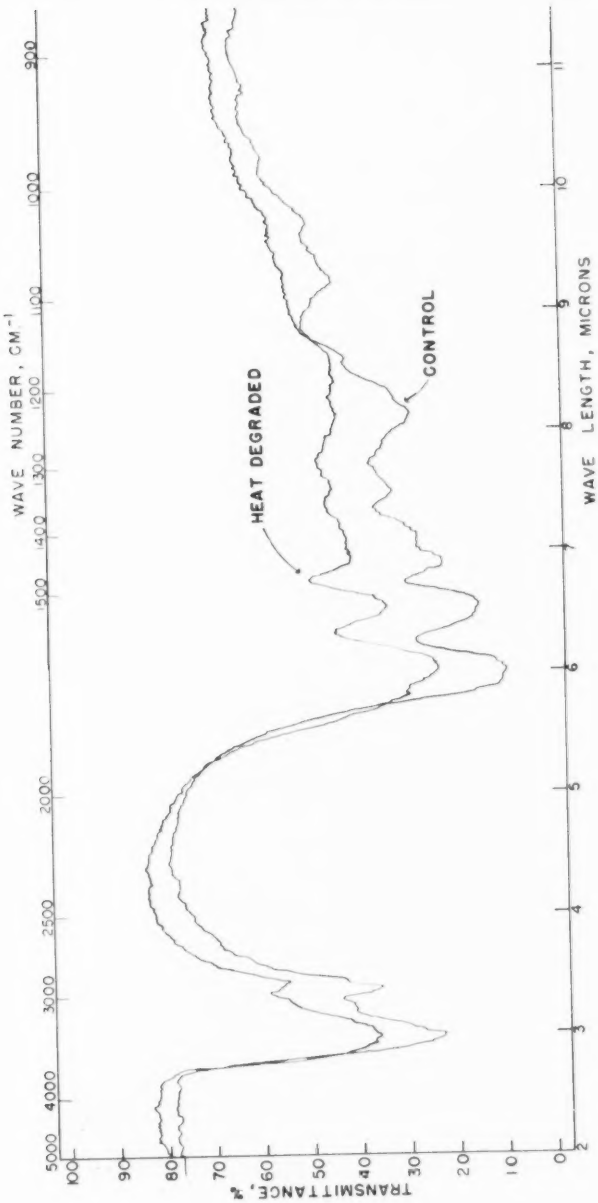

FIGURE 1.—Infrared spectra of collagen and of collagen heated at 170° in oxygen.

Table II lists the changes in the amino acid content caused by the several heating treatments. Only changes of 10% or more are recorded. The data in this table were obtained from a minimum of four chromatograms. The figures for tyrosine and hydroxyproline were obtained by specific colorimetric tests. Proline in some of the degraded materials could not be determined by the paper-chromatographic method because of interference by certain ninhydrin-reactive degradation products with similar R_f values. Figure 2 shows a typical chromatogram of a hydrolyzate of one of the more severely degraded materials.

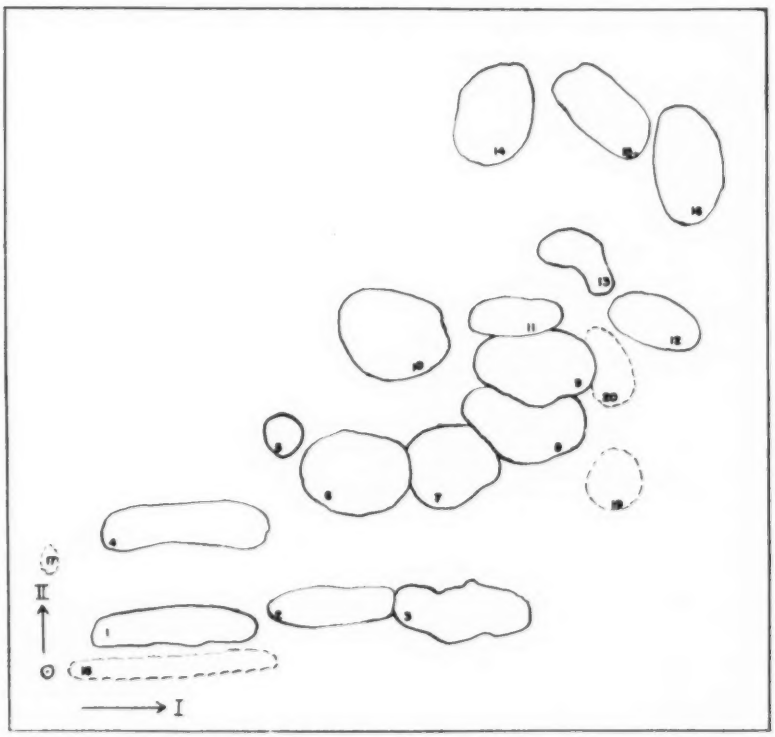

FIGURE 2.—Two-dimensional chromatogram of heat-degraded collagen hydrolyzate. Numbers 1–16 are amino acids observed in control hydrolyzate of collagen. Numbers 17–20 are ninhydrin-reactive products found only in hydrolyzates of the more severely degraded material. Solvent mixture I is 20:5:1 methyl alcohol, water, pyridine, and solvent mixture II is 10:10:5:1 tert-butyl alcohol, methyl ethyl ketone, water, and diethylamine.

To assist in visualizing the effects of oxygen, the data of Table II for collagen heated in vacuum and in oxygen are also presented in the bar graph of Fig. 3.

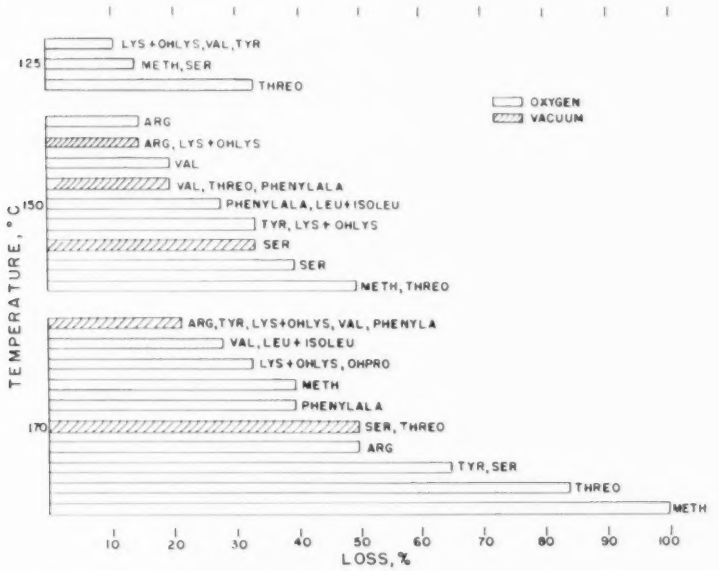

FIGURE 3.—Amino acid losses in collagen heated for 3 days, in vacuum and oxygen, respectively.

It is quite apparent from Table II and Fig. 3 that certain of the amino acid residues are more subject to attack than others. Aspartic acid, glutamic acid, glycine, alanine, and proline show little or no evidence of attack by any of the heating treatments, and hydroxyproline, leucine, and isoleucine were affected only by extreme heating in the presence of oxygen. In the native collagen these eight amino acids (calculated on a mole-fraction basis) account for 81% of the collagen molecule. If the amino acid content of the collagen sample heated for 3 days in oxygen at 170° C. is calculated on a mole-fraction basis, the mole fraction of the total protein structure which was affected by this most extreme degradation procedure may be determined. These data are given in Table III; they show that about 18% of the amino acid residues of collagen were so altered by the heat treatment that they were not determinable by the analytical procedures employed in this analysis. Of the amino acids attacked by the heat treatments, methionine, threonine, serine, and tyrosine are most severely degraded, and a considerable destruction of arginine and lysine occurs in the presence of air or oxygen at 170° C.

Over-all degradation is greatest in oxygen and least in vacuum. Three hydroxy amino acids (serine, threonine, and tyrosine) are most susceptible to oxidation.

TABLE III

CALCULATION OF MOLAR PORTION OF COLLAGEN STRUCTURE UNAFFECTED BY HEATING IN OXYGEN AT 170°C. FOR 3 DAYS

Amino Acid	Initial Mole Fraction	Loss %	Mole Fraction Unaffected
Methionine	0.006	100	0.000
Threonine	0.020	84	0.003
Serine	0.034	66	0.011
Tyrosine	0.006	65	0.002
Arginine	0.048	51	0.024
Phenylalanine	0.017	39	0.010
Lysine plus hydroxylysine	0.032	35	0.021
Valine	0.024	27	0.017
Leucine plus isoleucine	0.041	29	0.029
Hydroxyproline	0.090	32	0.061
Glutamic Acid	0.073	3	0.071
Aspartic Acid	0.047	0	0.047
Glycine	0.329	9	0.300
Proline	0.122	0	0.122
Alanine	0.107	8	0.099
			0.817

TABLE IV

WATER-VAPOR ADSORPTION OF COLLAGENS DEGRADED BY DRY HEAT

Rel. Hum. %	Control	Percent of Water Adsorbed					
		150° Preheat Treatment in			170° Preheat Treatment in		
		Vac.	Air	O_2	Vac.	Air	O_2
6	4.6	3.2	3.0	2.7	2.9	2.5	1.9
11	6.7	6.2	5.1	3.7	5.3	4.3	2.6
22	9.8	8.5	7.1	5.5	7.3	5.9	4.0
32.5	12.5	10.4	8.8	7.3	9.0	7.2	5.2
56	19.1	16.4	14.3		14.5	12.1	
75	27.1	23.5	20.2		20.5	17.2	

TABLE V

SOLUBLE NITROGEN DETERMINATIONS ON COLLAGENS DEGRADED BY DRY HEAT

Degradation Treatment	Percent of Nitrogen Dissolved in Extraction Lasting				
	1 min.	5 min.	1 hr.	8 hr.	16 hr.
Control	0	0	0	0	0
150°—Vacuum		1.7	2.7	2.8	2.8
170°—Vacuum		3.7	4.4	5.2	5.4
150°—Air	6.2	8.3	9.7	10.5	10.5
170°—Air	10.9	14.8	18.6	19.2	19.5
125°—Oxygen	5.3	5.2	5.6	5.6	6.2
150°—Oxygen	7.6	13.7	16.8	18.2	18.6
170°—Oxygen	5.2	11.1	21.5		26.2

TABLE VI

EQUILIBRIUM pH* OF COLLAGENS DEGRADED BY DRY HEAT
(*Three-day treatment*)

Heat Treatment	pH
Control	7.12
150°—Vacuum	5.70
170°—Vacuum	5.88
140°—Air	4.46
150°—Air	4.80
170°—Air	4.30
125°—Oxygen	4.81
150°—Oxygen	4.30
170°—Oxygen	3.50

*Determined after gentle agitation of 0.5 g. sample in 10 ml. of water for one hour.

Table IV gives the capacities for adsorbing water vapor of the thermally degraded samples. Each of the heated samples adsorbed less water vapor than the parent collagen. Heating the collagen in vacuum had the least effect on water-adsorption capacity, and exposure in oxygen produced the greatest change in this property. The reduction in water-adsorption capacity on heating collagen is thought to be a consequence of (*a*) a considerable loss (Table III) of polar side-groups by destruction or condensations and (*b*) changes in the over-all physical structures, e.g., a decrease in surface area.

The nitrogen contents of water-soluble fractions of the heat-degraded collagens are given in Table V. Heated samples, after reconditioning to

23° C. and 50% relative humidity, were extracted with water at 23° C., and the suspensions were filtered. Approximately 90% of the extractable nitrogenous materials were removed by extraction for one hour. Apparently a period of one hour in water at 23° C. was sufficient to break the majority of those bonds weakened during the heat treatment. Some of the differences in the rates of dissolution of the materials are ascribable to differences in ease of wetting. The amount of water-soluble nitrogenous materials parallels for the most part the amino acid destruction caused by the different heat treatments.

The equilibrium pH of the heat-degraded materials was determined in water with the glass electrode. The pH values of the solutions given in Table VI are the result of contributions by both the soluble and insoluble portions of the degraded materials. Each heat treatment produced a material more acidic than the untreated collagen, the most acidic being formed by heating in oxygen at 170° C. and the least acidic by the exposure in vacuum.

A portion of the collagen degraded by heating in oxygen to 170° C. was repeatedly extracted with portions of fresh water for 5 hours, during which time the pH of the extracts increased from 3.47 to 3.80 and their nitrogen contents approached zero. The extracted material was washed several times with acetone and then dried at 100° C. A nitrogen content of 17.80%, as compared with the initial value of 18.62%, was found. Some of this difference in nitrogen content probably represents loss in amide nitrogen from the heated material. The pH of the initial extract indicates that the equilibrium pH's of Table VI are mainly attributable to the dissolved portion of the degraded materials; this material is obviously acidic. Alteration of 35% (*see* Table II) of the basic amino acid side-chain groups (lysine and hydroxylysine) such as occurred during the exposure to oxygen at 170° C. would contribute greatly to a resultant acidic nature of the soluble, as well as of the insoluble, degraded material.

Further to characterize the water extracts, amino acid analyses, amino nitrogen determinations, and viscosity measurements were made. In Table VII are given the amino acid contents of (*a*) collagen heated at 170° C. in air for 3 days and (*b*) a water extract obtained by extraction of the same heated sample for 1 minute at 23° C. Inspection of Table V indicates that approximately 10% of the heated sample dissolved during the one-minute extraction. The extract was evaporated to dryness under reduced pressure, and the residue was hydrolyzed in the same manner as for the heated material. There is little difference between the amino acid content of the heat-degraded material and of the water-soluble fraction isolated from it. Thus, the heat treatment does not seem to have preferentially weakened certain bonds which, when broken during the water extraction, would split off non-parentlike fragments. This conclusion is also strengthened by colorimetric

TABLE VII

AMINO ACID ANALYSIS OF COLLAGEN DEGRADED BY DRY HEAT* AND OF ITS WATER EXTRACT

Amino Acid	Heated Collagen before Extraction %	Water Extract %
Arginine	5.6	6.4
Lysine plus hydroxylysine	3.0	2.2
Aspartic acid	6.6	6.5
Glutamic acid	10.5	10.7
Glycine	23.7	23.2
Serine	1.6	1.4
Leucine plus isoleucine	5.3	4.8
Valine	2.3	2.5
Methionine	0	0
Tyrosine	0.6	0.5
Threonine	1.3	1.0
Phenylalanine	2.4	1.6
Alanine	9.5	9.9
Hydroxyproline	12.7	12.3
Proline	15.1	14.8

*At 170° C. in air for 3 days

determinations of hydroxyproline made on water extracts of collagen degraded in oxygen and in air. The hydroxyproline solidus total nitrogen ratios of the heat-degraded samples did not differ sign ficantly from the ratios of those fractions removed from the degraded materials by extraction with water for periods of 1, 5, and 60 minutes. Since aspartic acid has been shown (8) to be preferentially liberated from a number of proteins by mild hydrolysis (100° C. for 1 hour in dilute acetic or oxalic acid), this amino acid might have been expected to appear in the water extracts as a free amino acid. No ninhydrin reactive spots were found on paper chromatograms of the water extracts prior to hydrolysis, which indicates th absence of any free amino acids in the extracts.

Intrinsic viscosities determined on the water extracts made 0.2 molar with respect to sodium chloride were in the neighborhood of 0.03. This is 5% of the viscosity of a purified gelatin solution and indicates the relatively small average size of the units in solution.

Ease of precipitation of water-soluble fragments with trichloroacetic acid (TCA) was also used as a measure of the size of units in the water extracts. At 1° C., trichloroacetic acid (15% final concentration) precipitated only 15% and 25%, respectively, of available, soluble nitrogenous material in 0.4% extracts of material heated at 170° C. in oxygen and in vacuum. Under exactly similar conditions gelatin was precipitated to the extent of 98%.

This, again, is an indication that the units in aqueous extracts of the materials degraded by dry heat are considerably smaller than the average molecule of gelatin.

TABLE VIII

AMINO NITROGEN DETERMINATION ON WATER EXTRACTS OF COLLAGENS DEGRADED BY DRY HEAT

8-Day Treatment	Water-Extraction Period	Amino N/Total N
150°—Air	5 minutes	0.022
	1 hour*	0.023
	16 hours	0.020
170°—Air	5 minutes	0.016
	1 hour*	0.015
150°—Oxygen	5 minutes	0.017
	1 hour*	0.016
170°—Oxygen	5 minutes	0.021
	1 hour*	0.020

*Sample extracted for 5 minutes was re-extracted with fresh water for one hour.

In Table VIII are listed the amino nitrogen total nitrogen ratios. The amino nitrogen data were obtained with the Van Slyke manometric equipment. Since a reaction period in the Van Slyke apparatus of 30 minutes did not increase the amino nitrogen values beyond that obtained in 5 minutes, the latter reaction period was employed throughout.

The amino nitrogen/total nitrogen ratio determined on solutions obtained by extracting the heated collagens for 5 minutes did not differ from that obtained on further extraction of the same sample. This suggests units of similar size in the successive extracts. The data of Table VIII include α and ϵ-amino nitrogen, but the ϵ-amino content (from lysine and hydroxylysine) of the soluble fractions is sufficient to account for almost all the amino nitrogen. Both precipitation with trichloroacetic acid and viscosity determinations indicate the presence of particles of relatively small size in the extracts. Since the data of Table VIII show that these small units are formed without the liberation of amino nitrogen, the chain scission occurring during the dry-heat degradation is oxidative, not hydrolytic.

Thermal degradation at 100° C. and various relative humidities. In Table IX are listed the total nitrogen values for samples degraded for 3 days in air at 100° C. at various relative humidities. The nitrogen contents of the degraded materials are slightly less than that of the parent, non-degraded collagen, but the greatest difference represents only a 1% change in nitrogen content.

TABLE IX

NITROGEN CONTENT OF COLLAGENS DEGRADED BY MOIST HEAT

Relative Humidity of Heat Treatment* (*approx.*) %	Nitrogen Value (*dry basis*) %
Control	18.15
80–90	17.95
72–78	17.93
65–70	18.00
50–60	18.10
20–25	17.94

*For 3 days at 100° C.

TABLE X

AMINO ACID RESULTS ON COLLAGEN DEGRADED BY MOIST HEAT

	Amino Acid Assay, %		
		Approx. Rel. Humidity of Heat Treatment, %*	
Amino Acid†	Control	72–78	80–90
Phenylalanine	2.9	2.5	2.1
Threonine	2.5	2.0	2.0
Methionine	1.0	0.6	0.6

*Treated for 3 days at 100° C.
†All amino acids were determined, but only those in which more than 10% loss occurred are listed.

In Table X data are given for three amino acids. On the basis of the chromatographic analysis these are the only amino acids which showed greater than 10% destruction upon heating the collagen at high humidity. Methionine, a relatively minor amino acid constituent, is attacked most severely. Phenylalanine and threonine are affected to a somewhat smaller degree.

In Table XI is given the capacity for adsorbing water vapor of the two samples most severely degraded by moisture-heat. The water-vapor adsorption of the heated samples is somewhat less than that of the parent collagen. The loss in adsorptive capacity is not much more than that observed in the collagens heated at lower relative humidities. Since little destruction of amino acids resulted from heating, even at the highest relative humidity, the decreased adsorptive capacity is probably caused by changes in physical state of the collagen. Kanagy and Cassel have shown that shrunken collagen has a considerably lower heat of wetting than native collagen. This correlated with a decreased capacity for uptake of water vapor (9).

TABLE XI

WATER-VAPOR ADSORPTION OF COLLAGEN DEGRADED BY MOIST HEAT

Relative Humidity of Heat Treatment,* (approx.) °C.	Water Adsorbed, Relative Humidity, %			
	6.0 %	11.0 %	22.0 %	32.8 %
(Control)	4.6	6.7	9.8	12.5
72–78	3.6	5.4	7.1	9.2
80–90	3.5	4.9	7.1	9.0

*For 3 days at 100° C.

TABLE XII

SOLUBLE NITROGEN DETERMINATION ON COLLAGENS DEGRADED BY MOIST HEAT

Relative Humidity of Heat Treatment,* (approx.) °C.	Percent of Nitrogen Dissolved in Extraction Lasting				
	1 min.	5 min.	1 hr.	8 hr.	16 hr.
Control	0	0	0	0	0
80–90	7.0	10.3	26.1		27.2
72–78	8.0	15.8	23.5	25.0	27.6
65–70	4.3	6.7	8.3	8.5	8.9
55–60					3.5
20–25					0.4

*For 3 days at 100° C.

The effect of relative humidity on the solubility of the degraded material is shown in Table XII. Higher humidity resulted in formation of more of the soluble nitrogen, with significant dissolution of collagen occurring only in materials heated at 50% or greater relative humidity. Solution of the degraded materials approached a maximum in one hour. The materials swelled considerably and appeared gelatinous. In contrast to the strongly acidic nature of the water extracts of the dry materials degraded by heat, the pH of extracts of collagen which had been degraded in the presence of moisture ranged from 5.1 to 5.7.

The intrinsic viscosities of aqueous extracts of the two samples most severely degraded by moisture-heat were approximately 0.10. This is one-sixth of the viscosity of a solution of purified gelatin and three times the value for extracts of the materials degraded in the absence of moisture.

These viscosities indicate that the particles dissolved by water from the collagen degraded by moisture-heat are units somewhat larger in molecular weight than those derived from the samples degraded by dry heat. This conclusion is also supported by the fact that slightly more than 60% of the nitrogenous material of the soluble fraction, derived from the collagen heated in a humidity of 80-90%, could be precipitated by trichloroacetic acid. This value of 60% is 2.5 times the maximum precipitation obtained on examining extracts of the materials degraded by dry heat. Under similar conditions 98% of the nitrogenous material of purified gelatin solutions was precipitated.

The hydroxyproline total nitrogen ratio of 1-minute, 5-minute, and 60-minute extracts of collagen degraded at the highest relative humidity did not differ from the ratio established for the unextracted, degraded sample. This indicates that solubilized portions of the degraded material were representative units of the parent degraded material. The average amino nitrogen/total nitrogen ratio as determined by the Van Slyke procedure on these extracts was 0.045. This ratio is twice the ratios of Table VIII and suggests that, on heating in the presence of moisture, chain scission mainly occurs by hydrolysis.

CONCLUSIONS

Heating collagen in oxygen, air, or vacuum to temperatures as high as 170° C. for a period of 3 days reduced the water-adsorption capacity and increased the solubility in water. Quantitative examination of the amino acid constituents of the degraded materials showed losses of certain amino acids. In particular, methionine, serine, threonine, and tyrosine were found in significantly reduced amounts in the heated materials. The greatest loss of amino acids occurred on heating in oxygen, with the least change being noted in vacuum experiments. Infrared spectra of the more severely degraded materials showed some small change from that of parent collagen in the region of the spectrum from 7 to 9 microns.

Heating collagen in air at 100° C. for 3 days at humidities varying from approximately 20% to 90% increased the solubility in water. Degradation, as evidenced by increased solubility in water and decreased capacity for adsorbing water vapor, increased as the humidity increased. Amino acid losses caused by heating at high relative humidity were very slight, only the methionine, phenylalanine, and threonine contents being significantly reduced. The water-soluble fractions obtained by heating collagen to the higher temperatures in the absence of moisture were of somewhat lower molecular weights than those of soluble fractions obtained by heat degradation in the presence of moisture. The chain scission which occurs during dry heating is of an oxidative type, whereas heating in the presence of moisture results mainly in hydrolysis.

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DISCUSSION

CHAIRMAN HIGHBERGER: This work represents a unique approach, so far as I am aware, to the collagen structural problem. I think one of Mr. Cassel's main objectives in this work was to learn something of the structural features of collagen.

Within the past two years it has become rather well established that the collagen molecule consists of three polypeptide chains having a total molecular weight of around 340,000. The individual chains in this unit are not necessarily the same in weight or in length. As a matter of fact, Dr. Doty at Harvard believes them to be of different lengths, and there is some pretty good evidence for this. These three chains are held together by hydrogen bonding between the peptide groups of the polypeptide chains.

Now in the ideal case the degradation of this material would involve the pulling apart or rupture of these hydrogen bonds and formation of what have come to be called "parent gelatin molecules." These are the undegraded polypeptide chains of which the original molecules are composed.

It seems that Mr. Cassel is doing considerably more than this in his degradative work. I was struck by the apparently small size of the units or fragments which he is getting in solution. The gelatin molecules would have a quite high average molecular weight—a hundred thousand at least—whereas apparently his fragments are considerably smaller than this.

I was also struck by the fact that apparently aspartic acid is not affected by his treatments, whereas it has been supposed, by virtue of other work, that aspartic acid is relatively loosely bound. If one merely mildly hydrolyzes collagen, aspartic acid is one of the first residues that shows up as being liberated.

I also wondered about this: I noticed that the most degraded specimen—the 170°, 3-day specimen—had a nitrogen content of 18.6%, which I consider to be the nitrogen content of pure collagen. I wonder if what you are doing is removing and degrading carbohydrate material.

MR. CASSEL: In other words, are we purifying the material?

CHAIRMAN HIGHBERGER: Yes.

MR. CASSEL: We are, obviously, removing something that does not contain nitrogen. I would hesitate to agree that we are simply removing carbohydrates through this process. Actually, the nitrogen on my purified collagen samples has never averaged as high as 18.6%. This 18.15% is about the average I get with this method of purification.

CHAIRMAN HIGHBERGER: It undoubtedly will depend on the process used for extraction. I am referring to very extensively extracted material.

DR. SHU-TUNG TU (United Shoe Machinery Corp.): Have you noticed any decarboxylation of collagen at higher temperatures?

MR. CASSEL: In this study we did not do any work to detect that. I think, though, that Dr. Kanagy has shown that CO_2 is removed from collagen when heated at higher temperatures.

DR. TU: As high as 170°? Or is that high enough?

MR. CASSEL: I am sure the 170° would be high enough for this length of time.

DR. KREMZER (General Foods Corp.): In a recent paper there was suggested the importance of the polysaccharide material in collagen and its relationship to the insolubility of collagen. Would you care to comment on this?

MR. CASSEL: I do not know the polysaccharide content of the material I was working with. Dr. Highberger had already commented on it. I do not know what influence it has. The control sample is insoluble in water. At least there is no significant solubilization. Whether that is due to a small amount of carbohydrate being left in there, I don't know, but I don't believe so.

CHAIRMAN HIGHBERGER: I might add that although the group with which I have been working was, I believe, the first actually to demonstrate the important effect of polysaccharide material in the reconstitution of collagen, I am rather skeptical about the role of polysaccharide material in native collagen in causing insolubility. We have data on skin material which has been so extensively extracted that you cannot detect more than an

extremely minute trace of polysaccharide material, and yet this is just as insoluble as other material which has more.

DR. KREMZNER: What was your source of collagen material? And what is your opinion as to why the proline and hydroxyproline were not affected at 170° C.?

MR. CASSEL: The source of the material was steerhide which was purified by a series of extractions but not exposed to any lime or trypsin treatments.

As to why the proline or hydroxyproline was not affected, hydroxyproline was attacked at the highest temperature, 170°, in oxygen. Why it was not attacked before we got to that point, I do not know. Proline should be a pretty stable amino acid. We would expect the hydroxyproline to be less stable. I think there has been some work done on the oxidation of individual amino acids. I do not recall that either one of those two were near the top so far as ease of attack is concerned.

TO THE ATOMIC SCIENTIST

Do you find it confusin',
When fishin' for fusion,
To get fission, when fusion is needed?
Do you e'er tear your hair,
With a rant and a r'ar,
When you find that your mission
Of tidying fission,
By the advent of fusion exceeded?
Do you ponder and wonder,
Midst the atom-burst thunder,
That rolls o'er New Mexico's dawn,
Will the world be made better,
Or warmer, or wetter—
Or will it just simply be gone?

[A similar] Indifference to domestic sources of raw materials governed the geography of leather manufactures. Tanning was so widely dispersed that in 1860 it ranked fifth among our industries in number of establishments. The latter were scattered through all parts of the country. Those of New England and the Middle States used many imported hides and averaged three times the capacity of tanneries situated in the South and West. Although fairly large plants, under corporate ownership and using mechanical improvements, were in existence early in the century, and numerous patents for leather-making processes and machinery were issued, no radical change occurred in tanning before the Civil War. Our most important leather-using manufacture was that of boots and shoes. Harness and saddle making remained a shop occupation.

—*History of Manufactures in the United States*, Vol. I, 1607–1860. Victor S. Clark. New York: McGraw-Hill Book Company, Inc., 1929.

LIFE LINES

Brief Biographies of Our Contributors

JAMES M. CASSEL—See the May, 1956, *Journal.*

PROFESSOR JOHN B. SPEAKMAN, D.Sc., F.R.I.C., F.T.I., is head of the Textile Industries Department of Leeds University, Leeds, England. Professor Speakman is generally recognized as one of the foremost authorities, if not *the* foremost, on the chemistry of keratin in general and of wool in particular. This recognition is attested by the many honors and awards that have come to him over the years. He is an Honorary Fellow of the Textile Institute and an Honorary Freeman of the Worshipful Company of Clothworkers; he holds the Warner Memorial Medal of the Textile Institute, the Research Medal of the Worshipful Company of Dyers (3 times), the Perkin Medal of the Society of Dyers and Colourists, the Grand Prix Littéraire of the International Wool Textile Organization, and the Gold Medal of Honor of the Verein der Textilchemiker und Coloristen.

Professor Speakman was educated at Manchester University (B.Sc., 1920; M.Sc., 1921). After a brief period of service as Research Chemist for the Chemical Warfare Committee of the British War Office he joined Leeds University as Lecturer in Textile Chemistry in 1924 and rose through the academic grades to a professorship in 1939. Most of his very numerous papers have appeared in such journals as the *Proceedings of the Royal Society*, the *Transactions of the Faraday Society*, and the *Journal of the Society of Dyers and Colourists*, but several of his stimulating addresses have appeared in the leather literature, particularly the *Journal of the Society of Leather Trades' Chemists*.

As leather chemists we are interested in the chemistry of keratin because we must remove the keratinous hair and epidermis from the skin. Professor Speakman's paper, however, has nothing to do with unhairing but should interest us for a much more significant reason. He has shown how the properties of wool fibers can be modified and improved by controlled chemical modification of their component protein. Perhaps the day may come when collagen fibers will be modified and improved by similar treatments. We could be more hopeful that this would come to pass if the leather industry had a man of Speakman's stature devoting his talents to this task.

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Proceedings, Reports, Notices, and News

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OBITUARY

JOHN J. MORAN 1893–1958

John J. "Jack" Moran died on July 2 after an illness of several weeks. He had been in the publishing business since 1919. For the last ten years he was an officer of Shoe Trades Publishing Company, publishers of the well-known trade journals *American Shoemaking* and *The Leather Manufacturer*. He became an Associate Member of our Association in 1943 and was invariably present at our annual meetings. The Association and particularly the editorial staff of this journal owe him a debt of gratitude for his help and cooperation. He will be missed.

ABSTRACTS

Volumetric Determination of Aluminum in Presence of Iron, Titanium, Calcium, Silicon, and Other Impurities. H. L. Watts. *Anal. Chem.*, **30,** 967–70 (1958).—The material containing aluminum is decomposed by acids or by a fusion, depending upon the type of material. Silica is removed as usual. Calcium is precipitated by adding $K_2C_2O_4$. The solution is brought to pH 11.5 by adding strong NaOH solution and then brought back to exactly pH 10.0, determined potentiometrically with an alkali-range glass electrode. At this point Al is in solution as aluminate, while the other metals have been precipitated as hydroxides, or oxalate in the case of Ca. Then add KF solution, forming AlF_3 and KOH, and titrate the liberated KOH to the pH 10.0 end point. The method is applicable to samples, or aliquots, containing 0.04 to 0.11 g. Al_2O_3.

H.B.M.

Swelling and Shrinkage Temperature of Tanned Collagen. B. N. Ghosh and S. Ghosh. *Bull. Central Leather Research Inst., Madras*, **4,** 176–80 (1957).—The forces of cohesion that resist hydrothermal shrinkage are analogous to viscous forces. From Flory's formula (*J. Phys. Chem.*, **46,** 870 [1942]) for the viscosity of a concentrated solution of a polyester, the authors deduce that the reciprocal of the shrinkage temperature, $1/T_s$, expressed in absolute temperature units (°K.) should be a linear function of the square root of the weight fraction, W_2, of dry leather in leather swollen at the isoelectric point. Measurements of T_s and swollen weight as a percentage of the dry weight were made on two sets of leathers: (1) collagen tanned with 0 to 10% HCHO, with T_s from 58° to 77°C., and (2) fully tanned Cr leather, partially dechromed with

boric acid (no dechroming), adipic, phosphoric, lactic, tartaric, and oxalic acids, with T_s from 124° to 61°C. Supposedly the Cr_2O_3 contents of these leathers declined in the above order, but no values for Cr_2O_3 content are given. No information is given as to how T_s values above 100°C. were obtained. Plots of $1/T_s$ (in °K.) against $W_2½$ were linear, as anticipated. H.B.M.

Studies on Proteases and Amylases as Unhairing Agents for Skins and Hides with Particular Reference to Reactions of Skin Mucoids with Amylases. S. M. Bose and W. Madhava Krishna. *Bull. Central Leather Research Inst., Madras*, **4**, 157–75 (1957).—Unhairing with madar latex (*Calotropis gigantea*) and the amylase of sprouted "ragi" (*Eleusine coracana*) has been described previously (*JALCA*, **50**, 192 [1955]; Indian patents 50806 [1953] and 52013 [1954]). This paper contains nothing further on actual unhairing, except a study of bactericidal agents that might be added to prevent putrefaction during the 1 to 3 days required for the enzymatic unhairing. The activitiy of madar latex was not impaired by adding boric acid, thymol, merthiolate, or toluene, and was destroyed or seriously impaired by adding I_2, *p*-nitrophenol, phenol, HCHO, $CHCl_3$ and Na benzoate. The activity of ragi extract was impaired or destroyed by all the above except merthiolate, toluene, and $CHCl_3$. The proteolytic activities of fresh latexes from 5 plants were measured with egg albumin as substrate using the modified Anson method (*JALCA*, **52**, 642 [1957]). Latex of madar was somewhat more active than latexes from papaya and fig; latexes of banyan and prickly pear have no proteolytic activity. The activity of madar latex showed large seasonal variations. No correlation was found between proteolytic activity and ascorbic acid, cysteine, or glutathione contents of the latex. The madar latex and proteases obtained therefrom lose activity rapidly on storage. Rate of loss of activity increases with temperature, is lowest at pH 7, and is somewhat decreased by adding reducing agents ($Na_2S_2O_4$, $Na_2S_2O_5$, Na_2S), possibly because loss of activity is caused by oxidation of sulhydril groups. Crude protease was obtained from madar latex by precipitation with alcohol. No preparation even approached satisfactory storage stability under any condition tried. The amylase activities of extracts of sprouted barley, ragi, and "jowar" were measured by determining reducing sugars liberated from starch. The barley extract was somewhat more potent than the ragi extract, but the latter is much the cheaper in India. Amylase was prepared from extract of sprouted ragi by precipitation with alcohol. Factors affecting its activity on goatskin mucoid prepared as described in *JALCA*, **50**, 192 (1955) were studied by mixing 5 ml. of mucoid suspension with 2 ml. of ragi amylase solution and determining the liberated reducing sugars, generally after 30 min. at 45°C. Activity was maximum at pH 4 and at about 52°C. The amount of reducing sugars liberated increased linearly with time up to 30 min., with concentration of mucoid up to 5%, and with concentration of enzyme up to 4%. The presence in the digestion mixture of 0.05% NaCl, KCl, NH_4Cl, $CaCl_2$, $BaCl_2$, or $MgCl_2$ increased the amylase activity by at most 6%. H.B.M.

Spectral Photometric Determinations of Potassium Chromic Sulfate Solutions. I. Changes during Heating. M. Zikmund. *Chem. Zvesti*, **11**, 528–35 (1957) (German summary); *Chem. Abstr.*, **52**, 7007*e*.

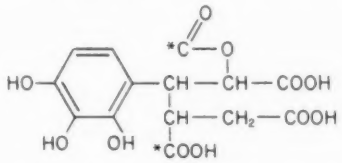
Determination of Tannic Acid and the Photometric Determination of Iron and Titanium. C. Yoshimura and K. Ono. *Nippon Kagaku Zasshi*, **78**, 320–23 (1957); *Chem. Abstr.*, **52**, 7022*d*.

The Mechanism of Keratinization of Human Epidermal Cells. A. G. Matolsky and S. J. Sinesa. *Anat. Record*, **128**, 55–67 (1957); *Chem. Abstr.*, **52**, 7379*c*.

Uronic Acids of Gelatin. A. M. Venet, J. Pouradier, and J. M. Landucci. *Bull. Soc. Chim. France*, **1957**, 1325–29; *Chem. Abstr.*, **52**, 7388*e*.

The Use of the Hydrolyzate of Tanned Hide Wastes for Feeding Purposes. J. Dusik. *Sbornik Ceskoslav. Akad. Zemedelskych Ved, Zivocisna Vyroba*, **2**, 1–14 (1957) (English summary); *Chem. Abstr.*, **52**, 7567*h*.

Chebulagic Acid and Chebulinic Acid. O. T. Schmidt. *Das Leder*, **8**, 106–10 (1957).—Chebulagic ($C_{41}H_{30}O_{27}$) and chebulinic ($C_{41}H_{32}O_{27}$) acids in the initial stages of hydrolysis take up one molecule of water to form the "neo" acids, neochebulagic and neochebulinic. The fact that optical rotation is not changed and the isolation of 2-methylglucose show that the ester linkage to the 2-hydroxyl of the glucose hydrolyzes to form the neo acids. Neither chebulagic nor neochebulagic acids split off CO_2 under conditions that will quantitatively decarboxylate gallic acid; therefore the chebulic acid portion of these molecules does not contain a free aromatic carboxyl. A structural formula for chebulagic acid is proposed; it consists of corilagin (1-galloyl-3,6-hexahydroxydiphenoyl-glucose) combined with chebulic acid by two ester links. Chebulic acid is a lactone of a tetrahydroxy-tetracarboxylic acid, and has the structure



In chebulagic acid the bottom (as shown) C atom marked with * is esterified with the 2-hydroxyl of the glucose of corilagin and the top C with the 4-hydroxyl. In neochebulagic acid only the ester with the 4-hydroxyl remains. The proposed structures for chebulinic and neochebulinic acids are the same as those above for chebulagic and neochebulagic except that 1,3,6-trigalloylglucose replaces corilagin. The trigalloylglucose was an amorphous substance with a rotation of $+27°$ in ethanol and no mutarotation. Chebulinic acid, on hydrolysis at 60°C. in acetone-water (1:3), first adds one molecule of water to form the neo acid which is a crystalline, dibasic acid melting at 193°–195°C. with decomposition, and a specific rotation of $+12°$ in ethanol. The neo acid then hydrolyzes to chebulic acid and trigalloylglucose and the latter to gallic acid

and 3,6-digalloylglucose. The hypothesis that two gallic acid groups attached to glucose combine in the plant by dehydrogenation to form hexahydroxydiphenic acid was tested with simple compounds. Gallic acid methyl ester was dehydrogenated to hexahydroxydiphenic acid methyl ester either by oxygen with platinum or animal charcoal or by anodic oxidation in slightly acid solution. In alkaline solution gallic acid splits off. Anodic oxidation also oxidized 1,4-digalloylbutanediol to 1,4-(hexahydroxydiphenoyl)-butanediol, and 1,2-acetone-3,6-digalloylglucose to 1,2-acetone-3,6-(hexadhydroxydiphenoyl)-glucose. In the last reaction, yield was small, but these dehydrogenation methods are not specific and other reactions predominate. I.D.C.

Automatic Equipment for Determination of Amino Acids Separated on Columns of Ion Exchange Resins. D. H. Simmons. *Anal. Chem.*, **30,** 1043–49 (1958).—This apparatus automatically collects 2-ml. fractions, adds the requisite amount of ninhydrin reagent to each, heats the fraction to develop color, dilutes the solution to the proper concentration, estimates the color spectrophotometrically, and records the results graphically. The machine approximately doubles the output of results obtained by the manual method, and analytical variations have been reduced by a factor of 3 over the manual method. H.B.M.

The Properties of Leather from the Scientific Standpoint. W. Grassman. *Das Leder*, **9,** 1–5 (1958).—The fundamental properties of leather, such as porosity, flexibility, and strength, depend on the fine microscopic structure and 3-dimensional weave of the fibers of the skin. The chemical and physical properties of the collagen fibers, which are proteins rich in polar groups, determine the breathing and the water vapor exchange characteristics of the leather. The scientist must devise methods for testing and characterizing these properties and cooperate with the tanner in improving his product. The leather promotion field includes improvement of quality, development of test methods, and self-regulation of the industry to maintain quality. I.D.C.

A New Tanning Procedure with Sulfite Cellulose Extract. A. T. Hough. *Rev. Tech. Inds. Cuir.*, **49,** 239 (1957).—A new tanning process of fairly recent conception—the first experiments were undertaken in 1950—has been perfected. The process makes use of a combination of lignosulfonate and urea-formaldehyde resin. The complex formed allows a tannage which is complete in itself and extremely rapid. The principle involved is derived from the fact that dimethylolurea and alcohols form ethers which are easily polymerized and have good tanning properties. It was deduced that the alcoholic groups of lignosulfonic acid would react with dimethylolurea to form a ligninyl-dimethylolurea ester of good tanning properties and easily polymerized within the hide fiber. It is well known that the ethers have better propensities than the methylolamines. The tannage can be carried out either with an extract prepared by condensing lignosulfonate, urea, and HCHO, or by applying the basic materials directly to the pelt without previous condensation. The mixture may be applied to pelt or to leathers already pretanned by other processes; or leathers tanned by the process may be finished by any other known tannage. T.D.B.

Effect of Diluents on Fusion Temperature of the Crystalline Regions in Plain and Tanned Cowhide. L. P. Witnauer and J. G. Fee. *J. Polymer Sci.*, **26,** 141–50 (1957).—Shrinkage temperatures, which are believed to be the melting points (T_m) of the crystalline regions in cowhide, were determined with the instrument described in *JALCA*, **51,** 530–41 (1956). Strips of dehaired, pickled, depickled, acetone-dehydrated cowhide, or of a commercial vegetable-tanned upholstery leather, or of cowhide tanned in the laboratory with 1% HCHO at pH 7.5, were dried in vacuum and then brought to various contents of water, ethylene glycol, phenol, or formamide. The shrinkage temperatures of these strips were measured in a mercury bath heated through a surrounding glycol bath. The temperature was raised by 3°C. per min. up to about 10° below the expected T_m and by 0.5°C. through the shrinkage range. The shrinkage was abrupt, and T_m was reproducible to 1°C. The same values for T_m were obtained when the final heating was done extremely slowly—3°C. in 4 hr. Results are given in the following table:

EFFECT OF DILUENTS AND DILUENT CONTENT ON MELTING TEMPERATURE (SHRINKAGE TEMPERATURE) OF PLAIN AND TANNED COWHIDES

Plain Hide

Glycol		Formamide		Phenol		Water	
Wt. %	t_m, °C.	Wt. %	t_m, °C.	Wt. %	t_m, °C.	Wt. %	t_m, °C.
25.0	103	12.5	106	17.5	115	24.5	97
29.5	97	14.0	100	27.0	96	25.5	95
36.5	85	21.0	87	29.0	96	33.5	84
42.0	85	21.5	86	31.0	92	34.0	82
		23.5	84	34.0	88	35.5	78
		30.5	75	34.0	88	36.0	80
				43.5	78	39.0	77
						48.5	63
						62.5	56
						Immersed	56

Tanned Hide

Vegetable*		Formaldehyde*	
% water	t_m, °C.	% water	t_m, °C.
0	120	26.0	98
11.5	97	29.0	94
16.5	89	30.5	92
19.5	85	35.5	83
24.0	84	Immersed	73
27.0	82		
35.5	79		
37.0	79		
Immersed	78		

* Based on total weight of hide, tannin, and water.

The reciprocal melting temperature was plotted against volume fraction of diluent. The data obtained for collagen–ethylene glycol by Garrett and Flory

(*Nature*, **177**, 176 [1956]) using a different technique fall on the same curve as the data obtained by the authors. By extrapolation to zero diluent the value 145°C. was obtained for the melting point of undiluted cowhide collagen, no matter which diluent was employed. This value could not be verified by heating dry cowhide collagen, which contracted only slightly and over a wide temperature range. Similar extrapolations to zero diluent gave melting points of 151°C. for HCHO-tanned cowhide, and 120°C. for vegetable-tanned cowhide. This last value was verified experimentally. At low diluent (water) contents T_m is as high, or even higher, for the tanned cowhide as for the plain cowhide, but at high diluent contents T_m is much lower for the plain cowhide. Indications are that HCHO- and vegetable-tanned cowhide when saturated with water contain only about 40% "effective" water, compared with about 62.5% for plain cowhide, due to cross-linking and blocking of active sites. The different effects of HCHO and vegetable tannin on the melting point of the dry material indicate a different mode of cross-linking. Heats and entropies of fusion and energies of interaction were calculated by the method of Flory *et al.* (*J. Polymer Sci.*, **12**, 103 [1954]). Heat of fusion was about 2000 cal/mole for cowhide, calculated from the data obtained with glycol, phenol, and formamide as diluents, but was 7000–8000 when calculated for cowhide and for the 2 tanned cowhides with water as diluent. Similar discrepancies were found in entropies of fusion, and calculated energies of interaction were erratic. These discrepancies cannot be explained at present. H.B.M.

Electroendosmosis through Hide and Leather Membranes. B. N. Ghosh and S. Ghosh. *Bull. Central Leather Research Inst., Madras*, **4**, 259–65 (1958).—Diaphragms of dehaired, delimed goatskin and various leathers were clamped between two limbs of a U-tube filled with solutions of various pH values. The diaphragms had been washed nearly free from electrolyte (after neutralizing to pH 7 in the case of Cr leathers) and then soaked for 3 days in the solutions of various pH values before being placed in the apparatus. Use of anions that form complexes with Cr was avoided. The arms of the U-tube were connected by a horizontal capillary containing an air bubble. Electroendosmosis was measured from the movement of this bubble when a potential was applied across the diaphragm. Zeta-potentials at various pH values were calculated from the Smoluchowski relation. The pH at which the zeta-potential was 0 was taken as the I.E.P. Values found for the I.E.P. were:

Limed, delimed goatskin	4.8
HCHO-tanned goatskin	4.5
Vegetable-tanned leather	3.25
Same, partly detanned with acetone	3.65
Cr leather (basic Cr sulfate tannage), dried before neutralizing	4.25
Same, not dried	7.5

These results confirm those of previous workers, including Otto's finding (*JALCA*, **46**, 147–49 [1951]) as to the effect of drying Cr leather on the I.E.P. The low I.E.P. of vegetable leather is ascribed to free acidic groups in the fixed tannin molecule. H.B.M.

Studies on the Enzyme Depilation of Hides and Skins. III. The Influence of Fundamental Culture Conditions on the Production of Protease and Depilatory Enzyme by Aerobic Bacteria. H. Toyoda and A. Futami. *Bull. Japanese Assoc. Leather Technol.*, **4**, 21–26 (1958) (English summary); cf. *JALCA*, **53**, 225, 295 (1958).—The effects of growth conditions on production of proteases and depilatory enzymes were studied employing strains of *B.megatherium* and *B. subtilis* isolated from hide. Protease I was measured by its effect on setting of gelatin, and protease II by formation of amino nitrogen. Some culturing conditions have different effects on production of proteases I and II, indicating that at least 2 proteolytic enzymes are produced. The effects of conditions on production of depilatory enzyme were more like the effects on production of protease I than protease II. Formation of protease II is more rapid than protease I, reaching a maximum in 3 to 6 days, while protease I increases slowly up to 9 days or more. Optimum pH is slightly below 7. Optimum temperature is 30°C. for *B. megatherium* and 35°C. for *B. subtilis*. Enzyme production increases with ratio of surface to volume of media (except when this ratio is excessively large), but agitation has little or no effect on protease production. Authors' summary (abridged)

Studies on the Change of the Composition of the Tanning Properties of Skin Tissue. I. Change of the Properties of Raw Skin during Storage. R. Sasaki and Y. Sato. *Bull. Japanese Assoc. Leather Technol.*, **4**, 16–20 (1958) (English summary).—The question whether there are changes in the property of raw skin during storage at 25°C. was investigated, and the experimental results are expressed statistically. The changes caused by salting or drying and by storage at 25°C. for various lengths of time were compared. In the case of salt-curing, some properties of alkali-treated skin, i.e., digestability by pancreatin and ability to combine with water, Cr_2O_3, and tannic acid were found to have changed, but ability to combine with HCHO was not affected. In the case of salting or drying treatment, the ability to combine with water was found to have increased, but absorption of Cr_2O_3 and tannic acid was decreased. The ability of salt-cured skin stored over a period of time to combine with water, Cr_2O_3, and tannic acid increased slightly between 1 and 4 months but decreased after 4 months. The increase and decrease were proportional. In the storage of dried skin the extent of the changes of the above properties was not the same, and the ability to absorb Cr_2O_3 and tannic acid was less when compared to fresh skin. In general the changes were small during a storage period of 1 to 4 months; however, it should be noted that properties of skin stored at 25°C. vary according to the length of storage. Authors' summary

Study of Leather for Gas Meter Diaphragms. I. Air Permeability. M. Kubota. *Bull. Japanese Assoc. Leather Technol.*, **4**, 27–32 (1958) (English summary).—The air permeability of sheep leather, measured by a modification of the method of Wilson and Lines (*Ind. Eng. Chem.*, **17**, 570 [1925]) was lower in the butt than in the belly. When the grain was removed, the permeability varied little with location. Chrome retanning made the leather softer and more uniform but increased the difference in permeability between butt and belly. Oil content was increased to a maximum of 65%. The customary application of excessive oil should be re-examined, since it is possible to render

the leather impermeable to air by coating with a waterproof layer. A different method of oiling to give more uniform absorption should be considered, as well as the effect of composition of the oil. Authors' summary (abridged)

Collagen. XI. Quantitative Examination of *in Vitro* Combinations of Collagen A–Mucopolysaccharide Acid. S. Bazin, A. Delaunay, and N. Briquelet. *Ann. Inst. Pasteur*, **93**, 624–30 (1957) (English summary); *Chem. Abst.*, **52**, 8228*f*.

Contribution to the Knowledge of the Fine Structure and Chemical Properties of Animal Connective Tissue Fibers. P. S. Santos, H. S. Santos, G. A. Edwards, A. R. Hoge, and P. Sawaya. *Mem. Inst. Butantan*, **27**, 1–25 (in English 27–39) (1955–56) (Pub. 1957); *Chem. Abstr.*, **52**, 8244*h*.

The Effect of Weak Organic Acids on the Rat Tail Collagen Fiber of Young and Old Animals. I. Banga. *Gerontologia*, **1**, 325–46 (1957); *Chem. Abstr.*, **52**, 8249*e*.

Collagen and Elastin: Effect of Age on Their Relation. D. A. Hall. *Gerontologia*, **1**, 347–63 (1957); *Chem. Abstr.*, **52**, 8334*c*.

Combined Treatment of Industrial and Domestic Wastes. L. S. Kraus. *Sewage and Ind. Wastes*, **30**, 199–207 (1958); *Chem. Abstr.*, **52**, 8428*b*.

The Reactivity of Keratin. R. C. Ghosh, J. R. Holker, and J. B. Speakman. *Textile Research J.*, **28**, 112–19 (1958).—The amorphous phase of wool contains and is created by amino acids with large side chains. These include those which are commonly used in cross-linking reactions. Since cross-linking is not likely to have a profound effect upon the elastic properties of a disorganized structure unless the degree of cross-linking is high, it is clear why cross-linking agents such as HCHO fail to give the desired effects on wool. It appears probable that the properties of wool could be modified advantageously by forming graft copolymers in the amorphous stage. It is suggested this might be accomplished easily by applying vinyl compounds to wool previously treated with maleic anhydride. R.M.L.

Estimation of Cortical Components in Various Wools. W. J. Thorsen. *Textile Research J.*, **28**, 185–97 (1958).—Wools of varying diameter and crimp, from several breeds and ages, were stained with various reagents chosen to give high contrast between the ortho- and the paracortical segments. Sodium plumbite yields a brown to black sulfide stain which is selective for the paracortex. Acid $Ni(No_2)_2$ preferentially stains the ortho segments, as does Br water. Solubility in aqueous urea and monothioglycol increases regularly with the degree of staining in the Ni solution. Finally, paralleling the staining behavior, the stress in the wool at 30% extension (wet) increases generally with diameter as well as with increasing maturity of the sheep. R.M.L.

The Amino Acid Composition of Keratins. D. H. Simmonds. *Textile Research J.*, **28**, 314–17 (1958).—Human hair, kid mohair, and two Merino wool samples (whose fiber diameter were the same but whose crimp frequency varied) were analyzed for amino acid composition, employing the Moore-Stein ion exchange chromatographic technique. Differences among the 4 samples were detected for the amino acids glycine, valine, leucine, cystine, and proline. Proline was the only acid which differed for the two Merino wools. R.M.L.

A Comparison of Fabric Tear Tests. Richard Steele. *Am. Dyestuff Reptr.*, **47**, 143–45 (1958).—The trapezoid, single-rip and double-rip tongue, Elmendorf, wing rip, and pin methods for the determination of fabric tear strength have been compared on cotton printcloth and sheeting treated with softeners. To emphasize the characteristic element of tear strength, which is the deformation of the fabric to distribute the applied load over its stress-bearing elements, the single-rip tongue test is the most satisfactory, followed by the double-rip tongue and the pin test. The other three tests are much less sensitive to the deformation factor in tear resistance. R.M.L.

Penetration and Supercontraction of Keratin Fibers by Lithium Bromide Solutions. A. R. Haly and June Griffith. *Textile Research J.*, **28**, 32–40 (1958).—Microscopic measurements were made of the diametral swelling and degree of supercontraction of wool fibers in LiBr solutions at room temperature. Supercontractions measured around the orthocortical and around the paracortical sides of the fibers differed. It was concluded that the epicuticle is an important barrier to the entry of the reagent. Supercontraction at 89° and at 100° C. takes place in two distinct stages separated by an intermediate period during which little or no contraction takes place. The first stage probably results from the breakdown of weak secondary bonds. The second contraction stage is well represented by an equation derived from a simple model; rate constants obtained by fitting this equation to the data show that there is a strong correlation between rates of contraction in the second stage and the relative humidity over the LiBr solutions. R.M.L.

The Effect of Sulfuric Acid on Wool. R. L. Elliott, R. S. Asquith, and D. H. Rawson. *J. Soc. Dyers and Colourists*, **74**, 173–80 (1958).—The attack of H_2SO_4 of various concentrations on wool has been examined under different time-temperature conditions of treatment. The attack has been shown to be of the following types: (*a*) hydrolysis in concentrations up to 44% H_2SO_4 by weight; (*b*) rapid dissolution which can be differentiated histologically from simple hydrolysis when the acid concentration is between 44% and 81.3%; (*c*) a slow attack between 93% and 98% which becomes considerably more rapid above 60°C.; (*d*) a rapid oxidative attack and dissolution in acid concentions in excess of 98%. Correlation of chemical, microscopic, and chromatographic data obtained from the action of concentrated H_2SO_4 showed that the attack is made first on the cuticle and indicates the presence of a considerable number of free hydroxy groups, which may arise from the serine and threonine residues of the cuticle or from the presence of polysaccharide. Removal of the cuticle sheath is followed by progressive dissolution of the fiber along with slow sulfonation of the amino acid residues containing benzene rings. R.M.L.

The Reaction of Formaldehyde with Wool and Its Effect on Digestion by Insects. J. R. McPhee. *Textile Research J.*, **28**, 303–14 (1958).—Formaldehyde at pH 12 combines with at least 95% of the indole, 55% of the primary amide, 45% of the guanidyl, and 40% of the primary amino groups of wool in 30 min. at room temperature. Wool treated in this way is resistant to the larvae of the clothes moth and the furniture carpet beetle, as well as to alkali, acid, thioglycollate, trypsin, and soil microorganisms; furthermore, physical properties such as appearance, felting shrinkage, bursting strength, abrasion resistance, and yarn strength are unaltered. R.M.L.

Vertical Fiber in Relation to the Properties of Chrome Side Leather. G. L. Amos. *J. Soc. Leather Trades' Chemists*, **42**, 79–90 (1958).—A small percentage of cowhides have a layer of vertically oriented (not to be confused with "high angle of weave") corium fibers below the thermostat layer in the butt region. Photomicrographs of sections taken from such hides at various steps in the tanning process show that vertical orientation persists and is not subject to modification by changes in tanning procedure. Dyes and fatliquors penetrate rapidly and extensively. Hides with vertical fibers yield soft leathers which lack fullness of feel but which have a fine break, poor lasting properties, notably low pressures at grain crack, and when pasted for drying, low distensions as measured with the lastometer. J.M.C.

Reversal of Double Refraction of Collagen Fibers by Tanning with Sumac Extract. A. Küntzel and E. Gratacos. *Das Leder*, **9**, 25–28 (1958).—A few tanning materials such as sumac and myrobalans under certain conditions are known to change the positive birefringence of collagen fibers to negative (*see* R. H. Marriott abstract, *JALCA*, **31**, 229 [1936]). An attempt was made to isolate a specific component of sumac that would cause this reversal of birefringence. Soaked, centrifuged hide powder was tanned with a 10% solution of a technical sumac extract (E_0), in a 20-volume float for 24 hr. The liquor was removed by suction, and the tanned powder was given two 30-second rinses with 30 volumes of distilled water. A portion (A_1) was dried in air and the remainder was extracted in a Soxhlet with methyl alcohol to give tanned powder (B_1). The extract (E_1), after removal of methanol, was taken up in water and used to tan a new lot of unchromed hide powder (A_2). The operation was repeated to give 4 unwashed powders (A series), 4 washed powders (B series), and 4 extracts (E series). Analyses of the extracts are shown in the following table:

Extract	Tannin	Nontannin	Insolubles
E_0	63.8	32.7	3.5
E_1	70.6	23.8	5.6
E_2	59.8	12.2	28.0
E_3	54.2	8.4	37.4

Purity and permanganate requirement both increased as the number of the extract increased. In all instances the unextracted leather powders (A series) had negative birefringence, and after extraction (B series) this returned to

positive. There was, therefore, no enrichment of a component which caused the reversal. Any fraction could cause the effect by being deposited on the hide powder in a water-soluble form in sufficient amount. The leather powders of the A series were softer and more leatherlike than those of the B series, although the B leathers contained more moisture in the air-dry condition. The greater water takeup by the B leather was the result of greater capillary volume; the inner surface area by the BET method (*J. Am. Chem. Soc.*, **60,** 309 [1938]) of the A leathers was 2.85 sq. m. per g., and of the B leathers 4.94 sq. m. In further experiments sumac-tanned leather was exhaustively extracted with water, then with 1:1 water-acetone mixture. Leather tanned with this acetone extract had negative birefringence before washing. The same result was obtained with a pure acetone extract obtained from sumac-tanned leather that had been thoroughly extracted with both water and methanol before the acetone extraction. The basic tannage was not important. Wattle-tanned leather retanned with sumac was negative, but washed sumac-tanned leather retanned with wattle was positive. The material that caused reversal of birefringence had the effect of a hydrate because either oven-drying to a moisture content less than that of the air-dry leather or soaking the leather in water made the optical effect disappear. I.D.C.

Stitch Tear Tests on Light Leather. C. D. Pomeroy. *J. Soc. Leather Trades' Chemists*, **42,** 90–100 (1958).—A study is reported of the effect on stitch-tearing loads of those factors considered likely to affect the failure of light leathers. Chrome calf and chrome-retan sheepskin were used. Steel wire was used to form the stitches, but waxed thread of similar diameter is said to prove equally applicable. The tearing load increases as the distance between stitch holes increases, but the rate of increase with increasing distance is not constant. A greater load is required to pull a stitch through from grain to flesh than vice versa. The thicker the wire, the greater is the load required. Tearing load increases as the distance of the stitch holes from the edge increases, and a maximum is reached when the stitch passes completely through the leather and does not tear out through the edge of the specimen. J.M.C.

An Approach to the Study of Vegetable Tannins by the Oxidation of Plant Phenolics. D. E. Hathway. *J. Soc. Leather Trades' Chemists*, **42,** 108–21 (1958).—The chemistry of the formation of large aromatic molecules of plant tissues is reviewed with particular emphasis on quinone-type structures, their reduction products, and reactivity. U. V. absorption spectra of products and a study of the oxygen uptake by polyhydroxy-flavans at 35°C. indicate that catechin autoxidation in neutral aqueous solution involves quinone polymerization but that constitutional differences modify this procedure for other hydroxy-flavans. Briefly reported is the *in vitro* transformation of gallates into ellagates under physiological conditions and the enzymatic oxidation of catechin to a polymer structurally related to some phlobatannins. J.M.C.

Shell Cordovan and Analogies of Combination-Tanned Sole Leather. W. Frankford and A. Finch. *J. Soc. Leather Trades' Chemists*, **42,** 122–31 (1958).—The paper discusses the various raw materials (butts) used in making

cordovan leather and the manner in which properties of "Shell Cordovan" are influenced by the fibrous structure of the horse butts used. Methods of tanning and finishing are outlined as are the advantages of this type of leather. Shortage of equine hides has triggered a search for means of producing Shell Cordovan from other type hides. Enzyme unhairing of cowhide was used in an attempt to obtain high fiber density. No likeness to the glassy layer of Shell Cordovan was produced by this procedure. Enzyme-unhaired bends tend to concentrate tanning material in the outer layers more than do conventionally limed hides. The leather produced from the enzyme-unhaired hides was attractive and flexible, resembling older-type sole leathers produced by unhairing hides by a sweating process. J.M.C.

Complexometric Determination of Sulfate. K. F. Sporek. *Anal. Chem.*, **30,** 1032–35 (1958).—Sulfate is precipitated as $PbSO_4$ from a solution containing 50% isopropyl alcohol, 10% concentrated HNO_3, and an excess of $Pb(NO_3)_2$ equivalent to about 0.05*M*. Under these conditions $PbSO_4$ is virtually insoluble and forms a coarse, rapid filtering precipitate. The precipitate is filtered through a fritted filter disk of fine porosity, leaving as much of the precipitate as possible in the precipitation flask, and washed 3 times with small amounts of 50% aqueous isopropyl alcohol. The precipitate is then redissolved in an excess of ammoniacal 0.1*M* EDTA solution (ethylenedinitrilo tetra-acetic acid) and the excess EDTA is back-titrated with standard 0.05*M* $ZnCl_2$ solution using Eriochrome Black T indicator. The method is highly accurate and is applicable to materials containing from 0.1% to 100% sulfate, though the analytical solution should preferably contain at least 0.1 g. SO_4 ion. The method is virtually free from interferences except that phosphate in rather high concentrations causes high results. The determination of sulfate by this method takes 30 to 45 min. compared with at least a day for the conventional gravimetric method. H.B.M.

Provisional Method (S.L.T.C.) for Testing the Fastness of Colored Leathers to Organic Solvents. *J. Soc. Leather Trades' Chemists*, **42,** 74–75 (1958).—A specimen of the leather in contact with a specified uncolored material is agitated in the solvent. The change in color of the specimen and staining of the uncolored material are assessed with the standard gray scale. **Provisional Method (S.L.T.C.) for Testing the Fastness to Rubbing of Light Leathers Wetted from the Back with Organic Solvents.** *Ibid.*, 75–77.—A sample is wetted from the back by contact with a felt pad soaked in the chosen solvent or mixture. The surface which is to be tested is then rubbed with a revolving dry felt pad, and the number of revolutions required to produce certain changes in the appearance of the finish is determined. J.M.C.

Preparative Fractionation and Quantitative Determination of the Portion of Synthetic Tanning Materials Precipitated by Metal Salts. A. Haglund. *Das Leder*, **9,** 29–34 (1958).—Vegetable tannins and syntans are complicated mixtures, so that different methods of analysis for tannin do not give the same results. Various metal salts do not all have the same ability to precipitate tannin. Lead salts precipitate nontannin as well as tannin. Zinc

and cadmium salts were found to be best for determining tannin, but to obtain complete precipitation it was necessary to buffer the solution, and for this purpose pyridine was chosen. The method was as follows: To 100 ml. of analytical solution containing 5–10 g. per l. of dry substance, add 5 ml. of 1*N* metal acetate solution, then add 2 ml. of pyridine dropwise with swirling, filter, pass H_2S through the filtrate for 20–30 min. to precipitate metal salts, filter, warm an aliquot (50 ml.) to remove H_2S, rinse into a tared dish, dry, and weigh. Nontannin can be determined in 45 min. with good precision. Corrections may be necessary because the syntan may contain Na_2SO_4 which is changed to the acetate by the metal acetate, or $(NH_4)_2SO_4$ which partially volatizes during drying. Instead of H_2S for removing metal salts Complexon III may be used, but with it results are less exact. The tannin values of syntans were much lower by the metal method than with hide powder. The ratios of purity by the zinc acetate method to purity by the hide powder method for a number of syntans ranged from 0.58 to 0.93 for exchange syntans, from 0.63 to 0.79 for white syntans, from 0.44 to 0.48 for pretanning syntans, and from 0.00 to 0.14 for bleaching syntans. Zinc salts precipitated more of a vegetable tannin than did cadmium salts, but the latter precipitated more of a syntan. The metal salt method is not proposed as a substitute for the hide powder method but as a valuable supplementary method. The nonprecipitatable component of various syntans was separated as follows for study: After adding metal salt and filtering, the filtrant was passed through a column filled with a hydrogen ion–saturated cationic resin to remove metal salts. The effluent was buffered to pH 3, and concentrated *in vacuo* at a low temperature. If the temperature is too high or the solution is too acid condensation will occur with formation of tannin. The washed metal precipitate was suspended in water, and then a cationic exchange resin saturated with hydrogen ion was added in small portions to set free the tannin. Resin is rapid and much better than H_2S for removing the metal. These tannin and nontannin preparations were used to tan calfskin. The tannin fraction made leather with a shrinkage temperature (T_s) 10° to 20° C. higher than that of the skin. The skin treated with the nontannin fraction was thin, empty, brittle, often translucent, and its T_s was not raised. Precipitation with metal salt and pyridine is a simple and exact method for fractionating tannin mixtures. The amount of syntan precipitated by either zinc or cadmium salts decreased as the degree of condensation decreased or the degree of sulfonation increased; this fact was determined with special phenol-formaldehyde condensates, condensed or sulfonated to various degrees. Mixtures of wattle and lignin extracts containing 10, 25, and 50% of lignin (total solids basis) were analyzed by the filter, the shake, and the zinc acetate methods. Zinc acetate precipitated 28–34% of the lignin that was present in the mixtures, although it precipitated none from pure lignin extract. Also the 2 hide powder methods showed more tannin than the percentage calculated from analyses of the components. The spent liquors from tan and combining value determinations were analyzed by the filter and the zinc acetate methods. The differences between results by these 2 methods increased from 2.5 to 28.0 as the proportion of lignin in the mixture increased from 0 to 50%. The material absorbed by hide powder but not precipitated by zinc was considered to be semitannin. A 1:1 mixture of wattle and lignin was separated into 2 fractions—fraction I, material precipitated by zinc, and fraction II, material not precipitated by zinc. Purities of fraction II were 44.5 by the filter method, 32.0 by the shake method, and 6.9 by the zinc method. Purities of fraction I by

the 3 methods varied from 83.8 to 89.8. Tan and combining values (24 hr.) were 88.6 and 63.4 for fraction I and 26.2 and 15.1 resp. for fraction II. In a tanning test fraction I produced a normal leather with T_s of 76° C., fraction II a hard, black, semitransparent product with T_s of 63° C. This tannin mixture had a high semitannin content, and semitannins hinder the tanning process.

I.D.C.

The Structure of Alpha-Keratin. M. L. Huggins. *Proc. Natl. Acad. Sci. U.S.*, **43**, 204–09 (1957); *Chem. Abstr.*, **52**, 8674*a*.

Mechanism of Formation of Chromium (III) Thiocyanate Complexes (Preliminary Communication). M. Beck and K. Toth. *Magyar Kem. Folyoirat*, **62**, 211–12 (1956) (English summary); *Chem. Abstr.*, **52**, 8821*b*.

Oxalates of Zirconium: Composition, Structure, and Properties. Heterometric Study. M. Bobtelsky and A. Ben-Basset. *Bull. Soc. Chim. France*, **1958**, 130–34; *Chem. Abstr.*, **52**, 8822*c*.

Oxalato and Malonato Complexes of Trivalent Metals. II. Stabilities of Trioxalato Complexes of Iron, Chromium, Aluminum, and Gallium. N. K. Dutt and B. Sur. *Z. Anorg. u. Allgem. Chem.*, **293**, 195–203 (1957) (in English); *Chem. Abstr.*, **52**, 8822*g*.

Reactive Groups of Collagen. I. Acylation and Guanidino Group Destruction. S. M. Bose and K. T. Joseph. *Arch. Biochem. Biophys.*, **74**, 46–58 (1958); *Chem. Abstr.*, **52**, 9257*g*.

Objective Color Measurements. I. W. Binder. *Melliand Textilber.*, **38**, 1398–1401 (1957). **II.** *Ibid.*, **39**, 77–80 (1958). **III.** *Ibid.*, 178–90; *Chem. Abstr.*, **52**, 9604*a*.

The Effect of Various Parameters on the Rate of Formation of Fibers from Collagen Solutions. H. B. Bensusan and B. L. Hoyt. *J. Am. Chem. Soc.*, **80**, 719–24 (1953).—Soluble collagen was prepared from very young calfskin, previously extracted with 0.1*M* NaCl, by extraction with 0.1*M* acetic acid. The extract was clarified by centrifuging, neutralized, and precipitated with NaCl (18%). The precipitate was suspended in water and lyophilized. Collagen solutions were made up to contain 0.10 to 0.15% protein in 0.1*M* NaCl, and dialyzed twice against 0.2*M* tris-(hydroxymethyl) aminomethane buffer, pH 8.1, containing 0.05*M* NaCl. The purity of the resulting solutions was tested by hydroxyproline assays, ultraviolet absorption spectra, and electrophoretic pattern. Rate of fiber formation when collagen solutions were mixed with buffer solutions containing various salts was studied by measuring the rate of increase in optical density at 290 mμ. The plots of optical density

against time are sigmoid curves, indicating a lag period followed by a period when optical density increases linearly with time. The end of this linear portion was taken as the end point. In the presence of salts, fiber formation was retarded. The order of decreasing effect exactly reversed the Hofmeister series for anions. In the case of cations the order of decreasing effect exactly followed the lyotropic series for the swelling of gelatin. Binding of ions by the collagen was studied from measurements of electrophoretic mobility. The inhibiting effect on coagulation increases with extent of binding. The retarding effect of salts is attributed to binding of ions of the salt at sites that take part in the coagulation reaction. However, as collagen is coagulated the collagen-salt compound in solution dissociates, and eventually all the collagen is coagulated. H.B.M.

The Reaction of Vegetable Tanning Extracts with Chromium Sulfate–tanned Collagen. K. H. Gustavson. *J. Soc. Leather Trades' Chemists*, **42**, 149–66 (1958).—The paper reaffirms the fact that pretannage of hide powder with cationic sulfate-Cr complexes markedly increases the irreversible fixation of vegetable tannin extracts—the degree of fixation varying widely between various extracts. Lightly prechromed hide powder (4–5% Cr_2O_3) shows much greater relative increases of additional fixation of vegetable tannin extracts than does more heavily chromed powder. The data indicate that the chromed hide powder binds vegetable tannin (1) by combination at normal vegetable tannin–protein sites, (2) by combination with additional basic groups freed on rupture of internal salt links caused by a discharge of carboxyl ions by Cr complexes, (3) by coordination of tannins on Cr atoms, (4) by displacement of sulfate groups in the Cr complex, and (5) by displacement of sulfate groups present as gegenions on the collagen–polyvalent Cr complexes. About half of the sulfate groups of chromed hide powder are easily displaced during vegetable retannage, while the other half appear more firmly bound, possibly due to their functioning as $-SO_4-$bridges between two Cr atoms. J.M.C.

The Assessment of the Colorfastness of Leathers. H. E. Nursten. *J. Soc. Leather Trades' Chemists*, **42**, 166–71 (1958).—Tests designed to distinguish leathers of high, medium, and poor colorfastness are discussed. The paper is concerned with fastness of leather to daylight, washing, water, perspiration, dry rubbing, wet rubbing, rubbing when wetted from the back with organic solvents, organic solvents, heat, water-spotting, and marking-off. J.M.C.

Determination of Amino Acids by Double Isotope-Dilution Technique. J. K. Whitehead. *Biochem J.* **68**, 662–68 (1958).—A double isotope-dilution method of analysis for amino acids in protein hydrolyzates obtained from small samples of proteins with acetic anhydride labeled with C^{14} and H^3 is described. Applicability of the method to analysis of insulin and chymatrypsinogen is shown. J.M.C.

Connective Tissue Growth Stimulated by Carrageenin. III. The Nature and Amount of Polysaccharide Produced in Normal and Scorbutic Guinea Pigs and the Metabolism of a Chondroitin Sulfuric Acid Fraction. H. G. B. Slack. *Biochem J.*, **69**, 125–34 (1958).—Growth of new

connective tissue was stimulated by injection of carrageenin beneath abdominal skin of guinea pigs. The granuloma tissue from scorbutic animals showed a greatly increased production of total polysaccharides in comparison to that of normal animals. Most of the increased polysaccharide production is due to greatly increased amounts of a fraction with properties similar to those of hyaluronic acid. J.M.C.

Separation of Amino Acids and Their N-Acetyl Derivatives by Paper Chromatography and Paper Ionophoresis. J. K. Whitehead. *Biochem J.*, **68**, 653–62 (1958).—An apparatus for two-dimensional paper ionophoresis or for one-dimensional paper ionophoresis to be followed by paper chromatography in a second dimension is described. A separation of 21 amino acids by two-dimensional ionophoresis and of 18 N-acetyl amino acids by one-dimensional ionophoresis followed by one-dimensional paper chromatography is given. J.M.C.

The Wool Protein Complex and Its Hydrothermal Instability. F. G. Lennox. *Proc. Intern. Wool Textile Research Conf., Australia, 1955 (publ. 1956)*, **B**, 22–34.—Frequent reference to wool chemistry in terms of "keratin" implies that the intricate histological constituents of the fiber are all built from a single protein—something that is difficult to conceive. Attempts are being made to resolve wool into individual proteins by methods causing minimum degradation. The major proteins located in the cortical cells resist extraction unless covalent bonds are split. Alkaline thioglycollate splits the -S-S- linkage, reducing both S-atoms, probably with little further change. The alkaline thioglycollate extract is shown by electrophoresis to contain 3 components, of which Component II predominates. By subjecting wool to a series of extractions in alkaline thioglycollate at pH 10.5 all the minor components and part of II are extracted, and further extraction at pH 12.3 yields II in a pure state. The extracted proteins represent 66% of the wool, and extracted II represents 41%. The extracted proteins come mainly from the cortical cells of the S (or ortho) segment. The molecular weight of II is about 32,000 at pH 7, and the compound appears to dissociate into units of molecular weight about 8,000 at pH 9. It contains less cystine but more dicarboxylic amino acids than parent wool. The amide content indicates that little degradation accompanies the solubilization process. When II is precipitated by acetic acid mild pressure causes the precipitate to become insoluble in alkaline thioglycollate, possibly because of conversion of the α- to the β- form. When wool is preheated in water before extraction with alkaline thioglycollate, the quantity of material extracted falls steadily with increasing temperature of pretreatment up to 120°C. and increases as the temperature of pretreatment is further increased. Hydrothermal degradation during the pretreatment itself begins at about 120°C. Dry heating causes less insolubilization than heating in water at the same temperature. A mixture of cortical and scale cells obtained by tryptic digestion released protein more readily than intact wool. Preheating this mixture of cells decreased the percentage of protein extractable by alkaline thioglycollate by almost half. This thermal insolubilization is thought to be caused by transformation of intramolecular into intermolecular H-bonds, diminished accessability of -S-S- links, and formation of lanthionine links. H.B.M.

The Electrophoretic Properties of Kerateine 2 (Compound II) and Some of Its Derivatives. J. M. Gillespie. *Ibid.*, **B,** 35–47.—Compound II (*see* preceding abstract) is designated as kerateine 2. Solubility–pH curves and electrophoretic behavior of this compound and its derivatives are studied. H.B.M.

The Preparation of Wool Protein Solutions. I. G. O'Donnell and E. F. Woods. *Ibid.*, **B,** 48–55.—Methods of dissolving wool without rupturing peptide bonds are discussed. The insolubility of wool is due to its high cystine content, together with interchain H-bonds and the presence of membranous sheaths that prevent egress of soluble proteins. The alkaline thioglycollate extracts of wool are very unstable. By repeated reduction and alkylation at neutral pH a stable product is obtained that is free from -S-S- links and is soluble in H-bond-breaking agents including alkali. Oxidation methods for attacking -S-S- links—even peracetic acid—are suspected of attacking peptide links. H.B.M.

Macromolecular Structure of Wool: The Terminal Amino Acids of the Fractions Obtained after Oxidation with Peracetic Acid. P. Alexander and L. F. Smith. *Ibid.*, **B,** 56–70.—Wool was oxidized with peracetic acid, and the resulting compounds, which are SO_3H compounds, were extracted with 0.1*M* and with 3*M* NH_4OH. Three fractions were obtained: β-keratose, the insoluble residue, supposed to constitute the cell membranes; α-keratose, precipitated at pH 4, supposed to constitute the micells or subfibrils; and γ-keratose, soluble at pH 4, supposed to constitute an interfibrillar cementing substance. Terminal amino acids were determined by the DNFB technique in whole wool and the three keratose fractions. Seven terminal amino acids—aspartic and glutamic acids, serine, threonine, glycine, alanine, and valine—were found in all four materials, though in varying amounts. Average calculated chain weights were about 86,000 for whole wool, 45,000 for β-keratose, 59,000 for α-keratose, and 28,000 for γ-keratose. The last figure is thought to be too high. The S contents of whole wool and of α-, β-, and γ-keratose are 3.63, 2.5, 2.2, and 6.13% respectively. H.B.M.

A Physicochemical Study of the Soluble Proteins from Peracetic Acid–Oxidized Wool. I. J. O'Donnell and E. F. Woods. *Ibid.*, **B,** 71–85.—The effect of pH, time, and ionic strength on electrophoresis, viscosity, and sedimentation has been studied for α-keratose (*see* preceding abstract). Electrophoresis does not, in general, indicate obvious heterogeneity, but sedimentation measurements reveal marked heterogeneity, which is interpreted in terms of aggregation-disaggregation phenomena. Addition of small amounts of sodium dodecyl sulfate simplifies the sedimentation pattern considerably. H.B.M.

Molecular Weights of Some Wool Keratin Derivatives. B. S. Harrap. *Ibid.*, **B,** 86–91.—Molecular weights, by the air-water interface surface tension method, were measured for kerateine 2 (a sulfhydril derivative), carboxymethyl kerateine 2, and α-keratose (a $-SO_3H$ derivative) under different conditions

of pH and ionic strength. The minimum subunit for all three compounds has a molecular weight of about 8,000. All compounds show aggregation under certain conditions of pH and ionic strength, which differ from one compound to another. H.B.M.

Observations on the Sorption of Acids by Wool. P. Larose and R. Donovan. *Ibid.*, **B,** 106–13.—Binding of HCl and H_2SO_4 by wool was measured by immersing wool in solutions of the acids (about 0.015*N*) and determining Cl, SO_4, and H ions in the equilibrium solutions. The sorption of HCl conforms to the Donnan theory better than to the Gilbert–Rideal theory, but sorption of H_2SO_4 can be explained equally well by either theory. These theories cannot explain the sorption of acid completely, since they do not apply to sorption of undissociated molecules. Wool sorbs 5.3 millimols gaseous HCl per g. (at 29°C.). This may be bound by amide groups, since silk and Nylon which contain amide groups likewise sorb large amounts of gaseous HCl, while Orlon and Terylene which have no amide groups sorb only negligible amounts. The sorption of undissociated acid by wool from aqueous solutions of monochloroacetic acid conforms to the Freundlich isotherm. H.B.M.

The Structure of Collagen Fibers. S. G. Tomlin. *Ibid.*, **B,** 187–92.—From data obtained by electron microscopy and low-angle X-ray refraction it is postulated that collagen is made up of long, thin cylindrical particles about 12 A in diameter. These contain *n* units, each about 640 A long. Each unit contains one "band" and one "interband" region. The band region (greater diameter) is thought to be the disordered region; it increases in length and becomes more orderly when the fiber is wet. The number of units, *n*, in the particle probably is 4, giving a length of about 2900 A for the particle. The interbands occupy sites on a transverse hexagonal lattice. The band ends of particles are inserted into interstitial positions in what would otherwise be a perfect hexagonal array. Such a structure is shown to be in agreement with the observed equatorial X-ray spacings of wet and dry collagen. Variations in arrangement account for axial periods that are multiples of 640 A. This discussion is wholly geometrical. H.B.M.

Some Possible Modifications of the Alpha-Helix and Speculations on the Possibility of Intrachain Disulfide Bonds in Alpha-Keratin Structures. H. Lindley. *Ibid.*, **B,** 193–201.—The Pauling–Corey α-helical structure, consisting of 7 chains coiled about an axis that is itself helical, forming a superhelix or coiled coil, conforms to X-ray data for α-keratin. However, the presence of numerous interchain disulfide links in such a structure does not harmonize with the easy extension of the fiber from the α- to the β-form. By analogy with insulin and chemical evidence for the presence of 2 types of disulfide linkages, it is suggested that part of the disulfide links are intrachain, and further that the sense of the superhelix may be reversed periodically. H.B.M.

X-Rays and the Stoichiometry of Keratin: A Renewed Enquiry. W. T. Astbury. *Ibid.*, **B,** 202–19.—An attempt is made to correlate the data from

X-ray diffraction measurements with amino acid composition of wool. Different natural mammalian keratins differ chiefly in their cystine contents. It is suggested that the polypeptide that forms the fundamental α- helix is quite low in cystine and that the major part of the cystine is embodied in a kind of cementing substance. From the macroperiod along the fiber axis of α-keratin (198 A), and the length of a single amino acid residue, it is calculated that there are 133 (or 132) amino acid residues per period. Ignoring cystine and proline, the amino acid distribution, as between acid and basic amino acids, hydroxy and phenolic acids, "light inactive" and "heavy inactive" acids, gives indications of a subunit one-twelfth as long as the macroperiod (11 amino acid residues). Attempts will be made to correlate possible arrangements of amino acids with the intensity of different orders of the meridional X-ray reflections. H.B.M.

In Praise of Wool. W. T. Astbury. *Ibid.*, **B,** 220–37.—This is a highly interesting address by the pioneer worker in the field of protein fiber structure. This is not a piece of propoganda but rather an exposition of the extensive advances in our knowledge of the structure of all the fibrous proteins that can be traced back to the early studies on the X-ray diffraction diagrams of wool and other keratinous materials. These discoveries embrace matters as diverse as the mechanism of contraction of bacterial flagellae and the modern method of permanent waving. H.B.M.

Principles of Chromatography. R. L. M. Synge. *Ibid.*, **B,** 238–48.—A review, by one who received a share of a Nobel Prize for his studies in this field. The occasion for the lecture is that "on matters of principle none of the textbooks in the English language seem (to the author) to give a sufficiently clear picture." H.B.M.

BOOK REVIEW

Gerbereichemie und Gerbereitechnologie. Fritz Stather. 3rd ed. Berlin: Akademie-Verlag. 1957. 948 plus xxvi pp.; 239 illustrations. Cloth. 88DM.—The editions of 1943 and 1951 were reviewed in *JALCA*, **45,** 762 (1950) and **49,** 66 (1954). The increased pace of scientific and technological progress in the tanning field as well as some changes in theoretical viewpoints has made the revision of the second edition desirable. The appearance of 3 editions within 9 years reflects, however, not only the author's determination to keep his textbook in line with new developments; it is also an evidence of the fine reception which the previous publications have met. This edition can indeed be considered a most up-to-date and comprehensive text on leather chemistry and technology. It contains 230 pages and 44 illustrations more than its predecessor. Great care has been taken to improve the type as well as the selection and quality of the illustrations and graphs. Many sections have been practically rewritten, such as the ones on sources of supply for cattle hides, tannery effluents and their disposal, the chemical constitution of vegetable tanning materials, synthetic tanning materials and their application, the chemistry of

complex compounds, wetting and emulsifying agents, and plastic finishes. A new and very welcome addition is a brief chapter dealing with the utilization of leather in the manufacture of shoes and many other kinds of leather goods. The division of the text into 6 sections has been maintained. The sections are subdivided into 32 chapters. An enumeration of the headings of these chapters will familiarize the reader with the organization and scope of Dr. Stather's book.

SECTION I. Raw hide and its conservation, 141 pages. (1) Microscopical anatomy and histology of the animal skin. (2) Technology of the animal skin. (3) Chemistry of the animal skin. (4) Preservation and disinfecting methods.

SECTION II. Operations of the beamhouse, 110 pages. (5) Water and effluents in the tannery. (6) Soaking of the raw hide. (7) Loosening of the hair and opening of the hide. (8) Mechanical and other beamhouse operations. (9) Deliming. (10) Bating. (11) Byproducts of beamhouse operations (this chapter includes the manufacture of sausage casing and of artificial horse hair).

SECTION III. Tanning agents and processes, 279 pages. (12) Vegetable tanning materials. (13) Tannage with vegetable tanning materials. (14) Synthetic tanning agents and their application. (15) Lignin extracts and their application in tanning. (16) Chrome tanning agents and chrome tannage. (17) Alum tannage, iron tannage, other mineral tannages. (20) Tanning theories.

SECTION IV. Leather-finishing materials and methods, 163 pages. (21) Washing, bleaching, and degreasing of leather. (22) Lubricating materials and procedures. (23) Leather dyes and coloring methods. (24) Finishing materials, pigment finishes, lacquers, japanning. (25) Mechanical finishing operations.

SECTION V. Variety of leathers and leather properties, 128 pages. (26) Commercial leathers. (27) Properties of finished leather. (28) Defects on finished leather. (29) Chemical and physical testing of leather and evaluation. (30) Storage and utilization of leather; leather preservation and care.

SECTION VI. Fur skins and fur dressing, 50 pages. (31) Histology and technology of furs. (32) Fur dressing and improvement of furs.

The book concludes with brief descriptions of a great number of commercial products (mostly German) for the tanning and fur dressing industries. Dr. Stather's book is carefully written and as complete as one can expect considering the size of this volume. It contains an abundant number of references to the international literature up to and including 1956. A number of errors, some carried over from the previous edition, are to this reviewer the only object of criticism (minor). Dr. Stather's excellent work can be highly recommended to everyone who is interested in our professional field and who is familiar with German. It will offer valuable service to the student as well as to the educated tanner.

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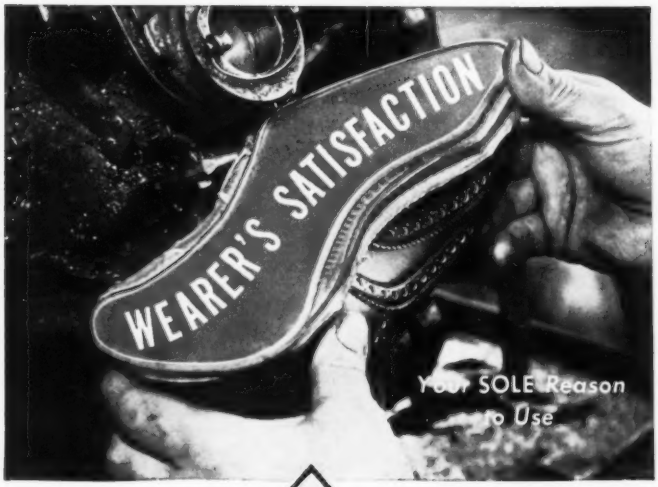

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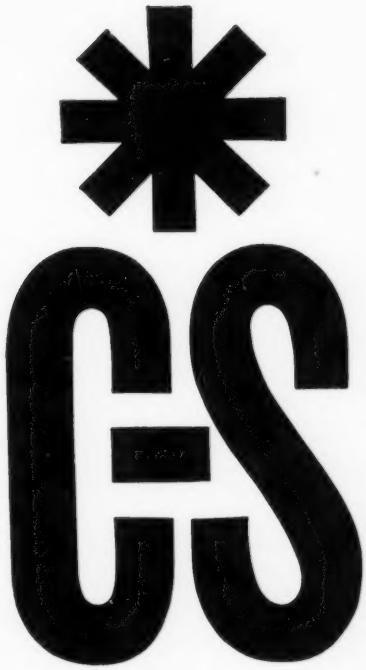

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